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# CHEMISTRY AS APPLIED



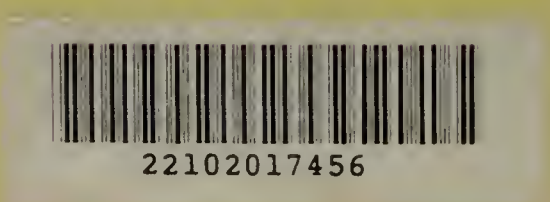
TO

# THE ARTS & MANUFACTURES

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# CHEMISTRY,

## THEORETICAL, PRACTICAL, AND ANALYTICAL,

AS APPLIED TO THE

## ARTS AND MANUFACTURES.

BY

WRITERS OF EMINENCE.




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# COWLES CANDLE MOULDING MACHINE.

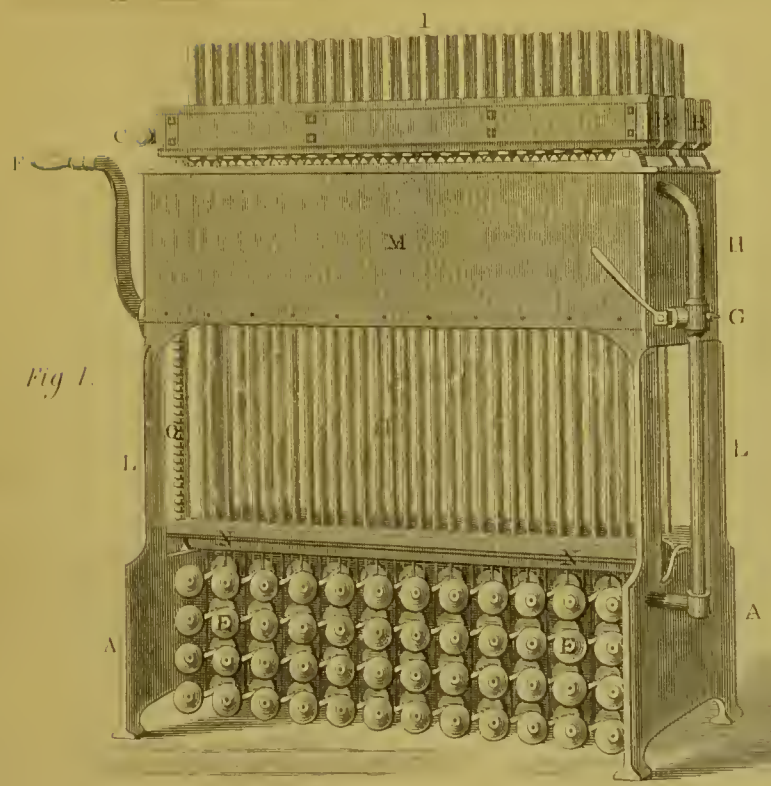



Fig 1.

Fig. 3.

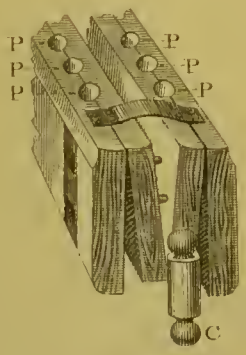
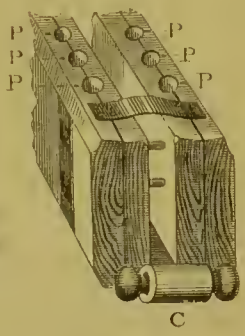



Fig 4.





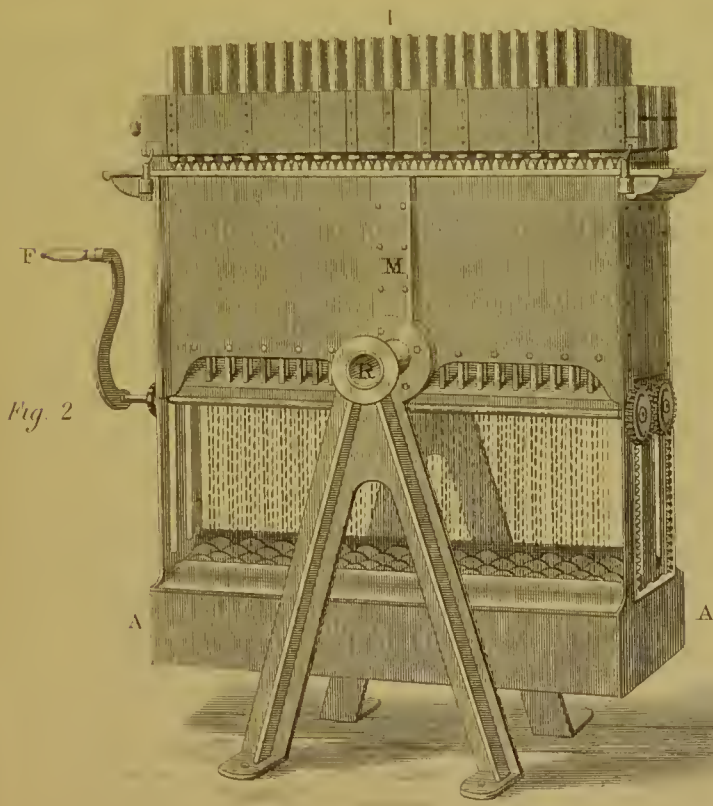




Fig. 2

Fig. 6.

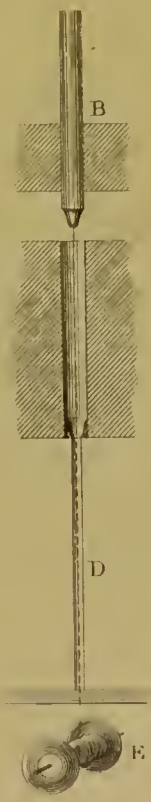
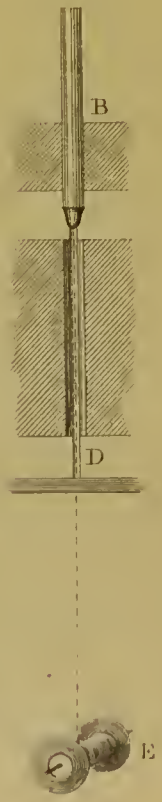
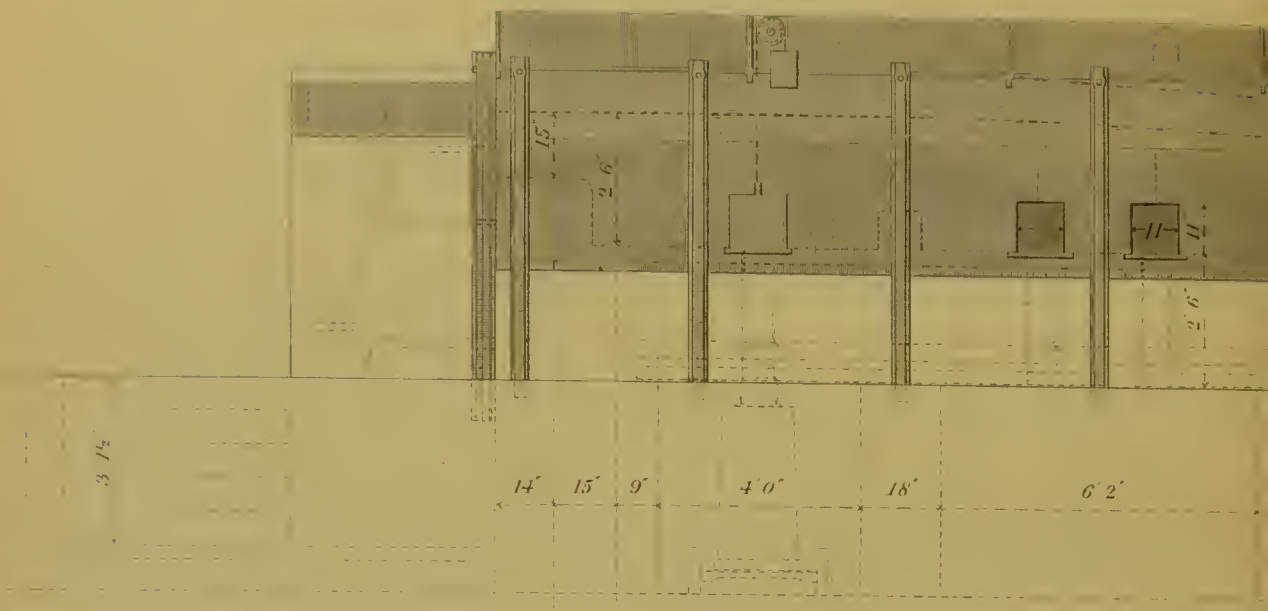
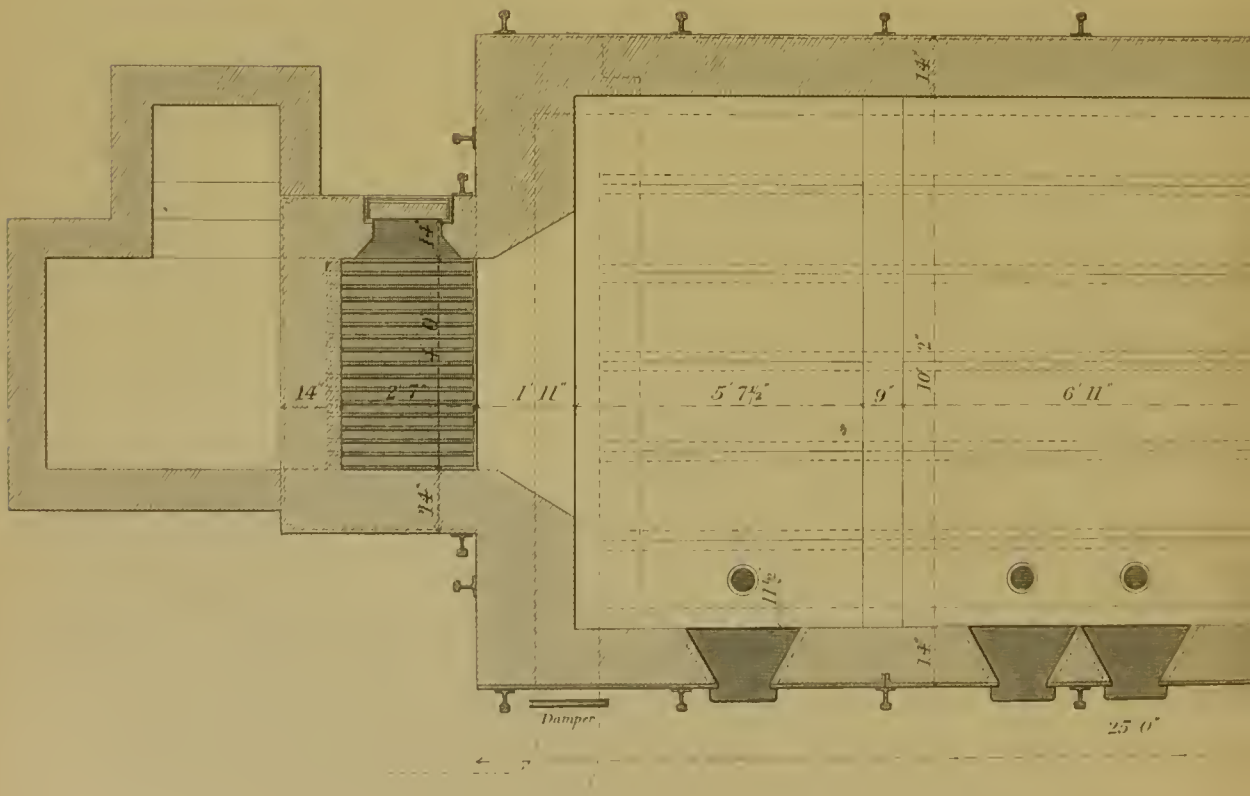
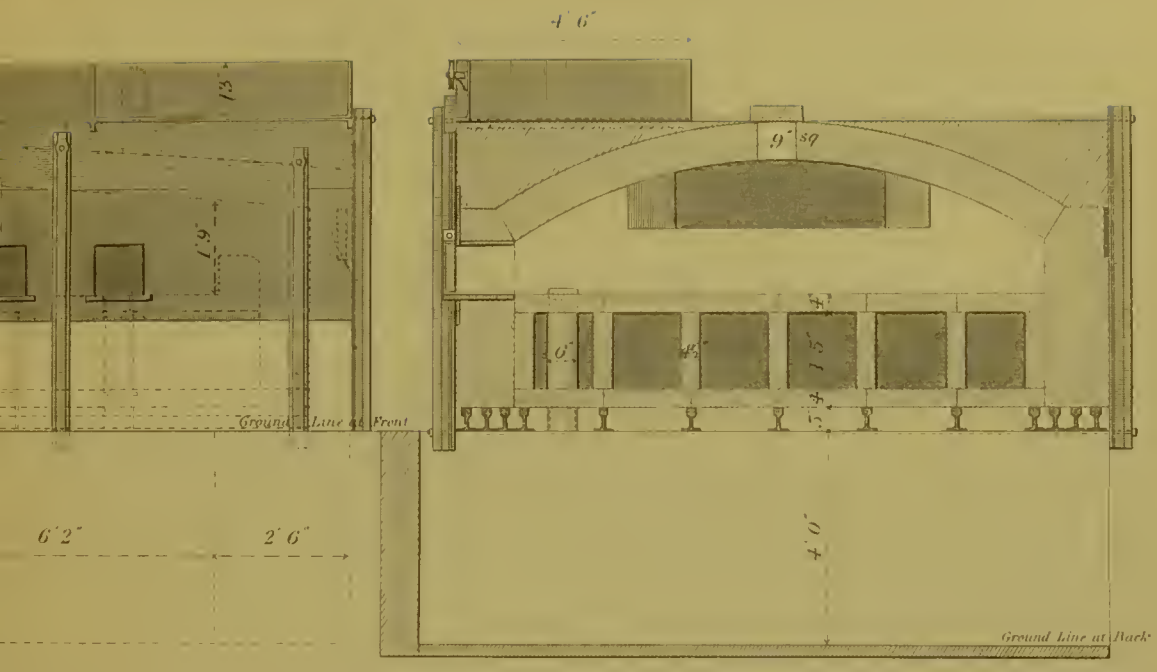


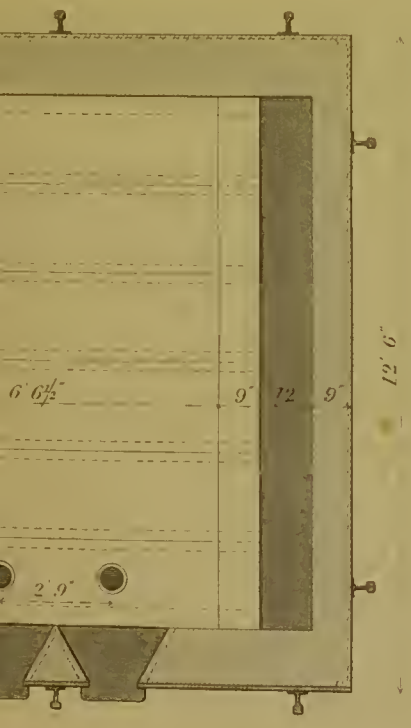

Fig. 5




15"
2' 6"
11"
11"
2' 6"
3 1/2
14"
15"
9"
4' 0"
18"
6' 2"


14"
14"
2' 7"
14"
1' 11"
5' 7 1/2"
9"
10"
2"
6' 11"
11 1/2"
14"
Damper
25' 0"



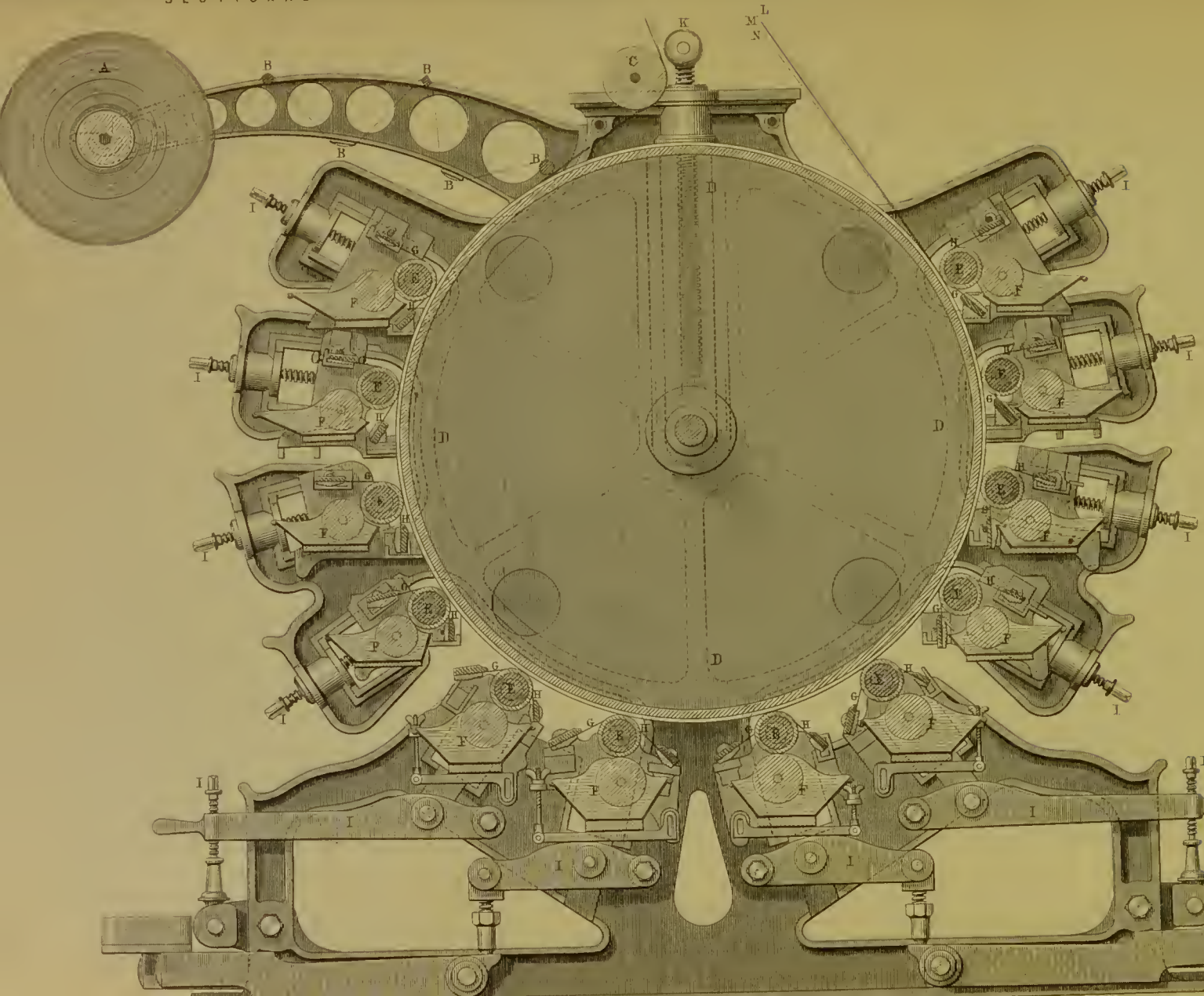

SPONGY IRON FURNACE.

Scale of Feet

1 2 3 4 5 6 7 8 9 10 11 12 Feet

& GLASGOW

SECTIONAL ELEVATION OF TWELVE COLOUR MACHINE BY THOMAS [illegible]



REFERENCE.

A *Piece in Roll to be printed.*

B *Rails for Stretching and Straightening same before entering Machine.*

C *Breast Roller.*

D *Main Cylinder of Machine.*

E *Copper Engraved rollers with portions of Pattern.*

F *Colour furnishing Rollers and Boxes.*

G *Doctors for removing superfluous colour from surface of Engraved Rollers.*

H *Doctors for removing Lint adhering to Copper Roller, after leaving colour upon cloth.*

I *Screws and Levers for setting up engraved Copper Rollers and appendages.*

K *Screws for regulating position of Main Cylinder.*

L *Piece printed leaving Machine for drying.*

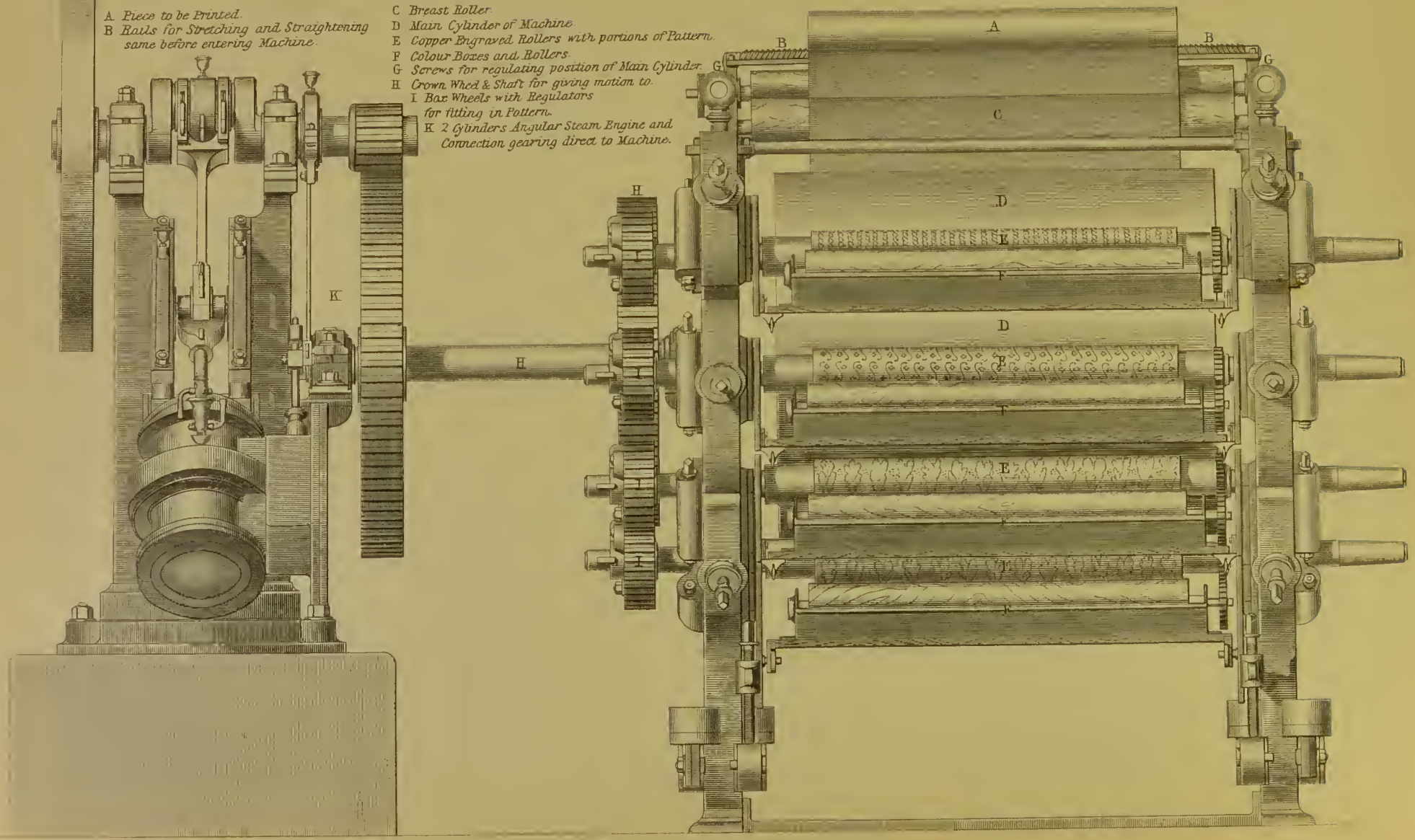
M *Blanket.*

N *Grey.*

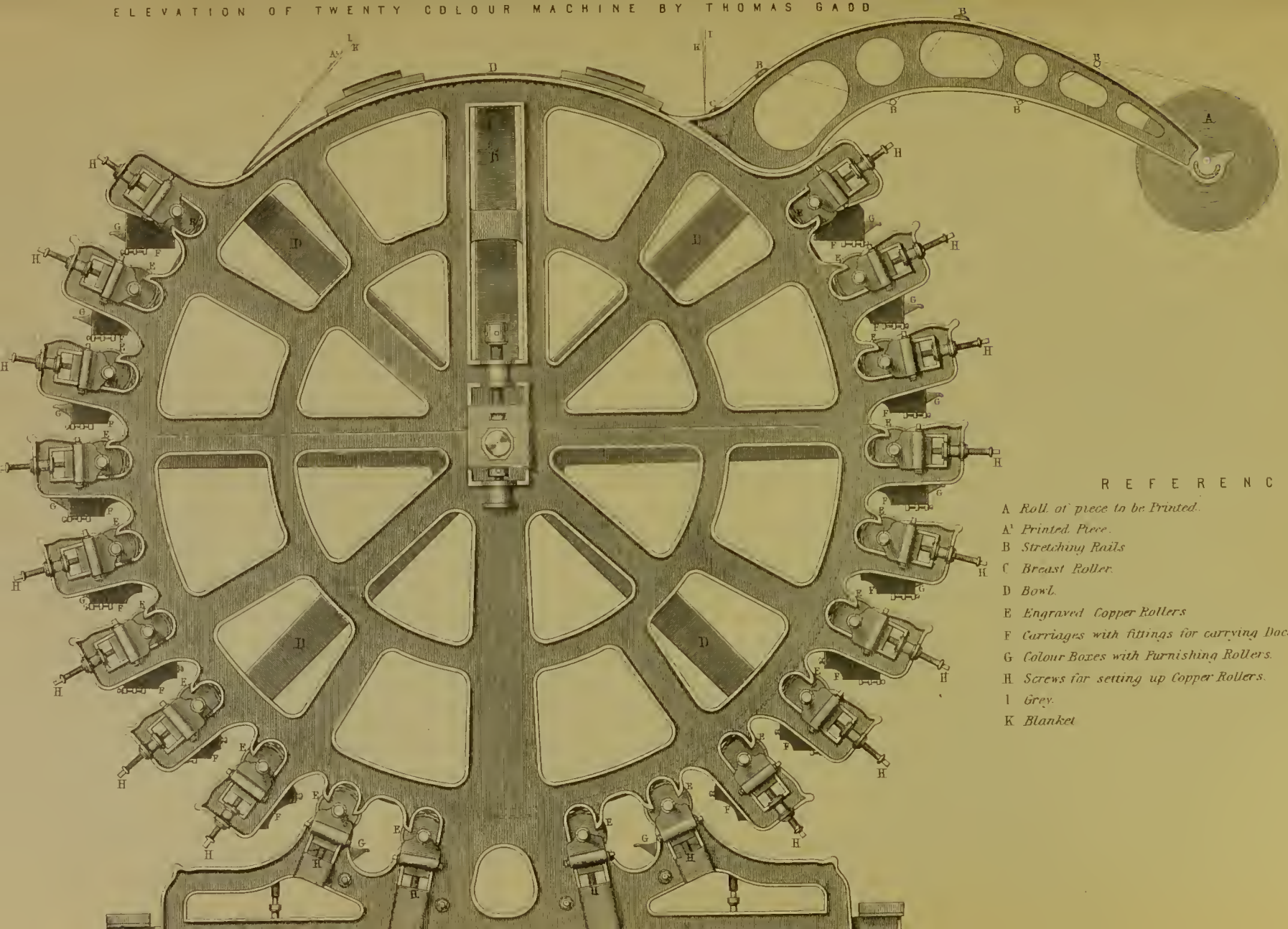
FRONT ELEVATION OF EIGHT COLOUR MACHINE BY THOMAS GAOD.

REFERENCE.

A. *Piece to be Printed.*
B. *Rolls for Stretching and Straightening same before entering Machine.*
C. *Breast Roller.*
D. *Main Cylinder of Machine.*
E. *Copper Engraved Rollers with portions of Pattern.*
F. *Colour Boxes and Rollers.*
G. *Screws for regulating position of Main Cylinder.*
H. *Crown Wheel & Shaft for giving motion to.*
I. *Bar Wheels with Regulators for fitting in Pattern.*
K. *2 Cylinders Angular Steam Engine and Connection gearing direct to Machine.*



ELEVATION OF TWENTY COLOUR MACHINE BY THOMAS GADD



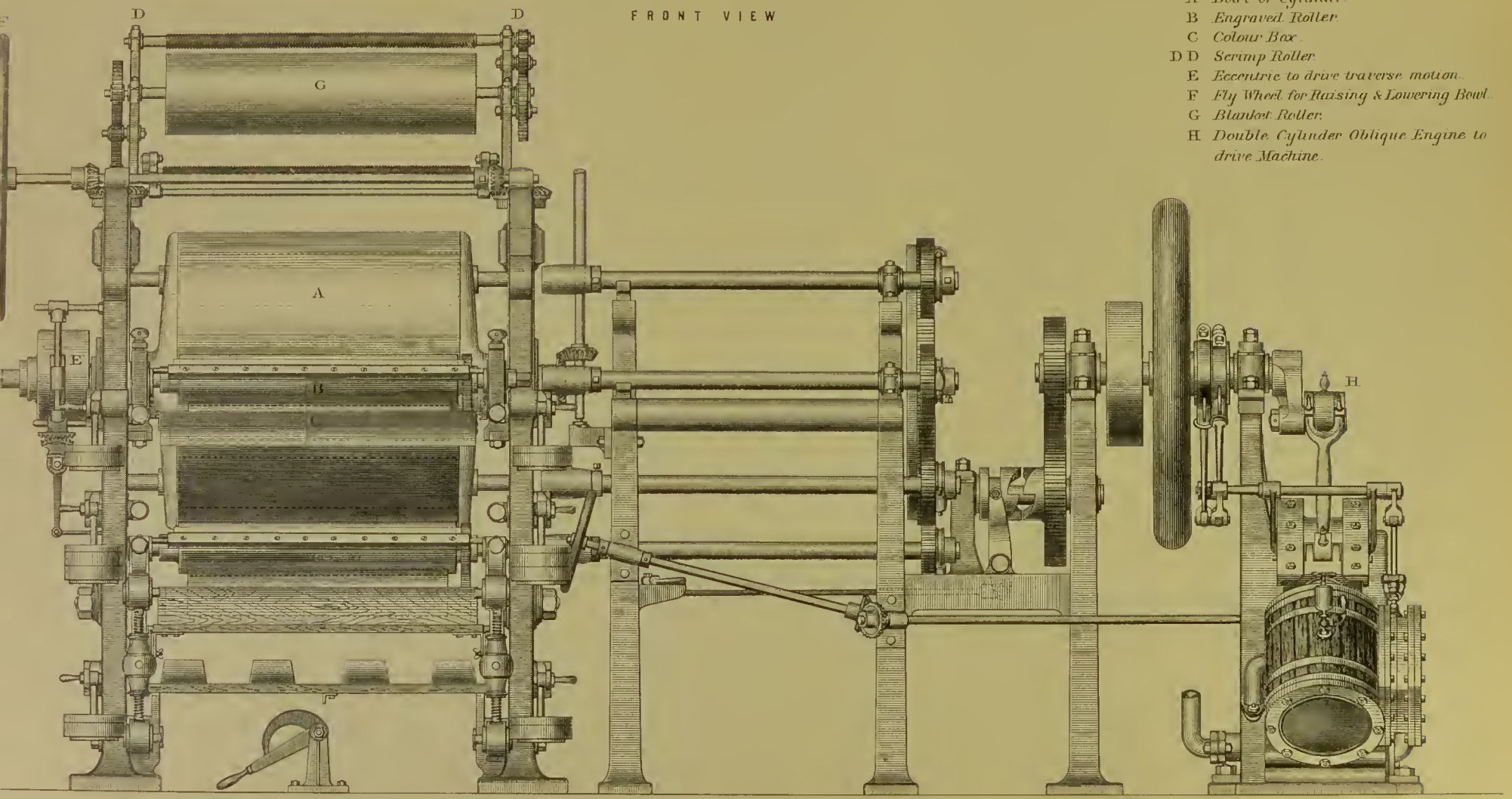
REFERENCE.

A *Roll of piece to be Printed.*
A¹ *Printed Piece.*
B *Stretching Rails.*
C *Breast Roller.*
D *Bowl.*
E *Engraved Copper Rollers.*
F *Carriages with fittings for carrying Doctors and Colour Boxes.*
G *Colour Boxes with Furnishing Rollers.*
H *Screws for setting up Copper Rollers.*
I *Grey.*
K *Blanket.*

# EIGHT COLOUR PRINTING MACHINE BY TULPIN FRERES.

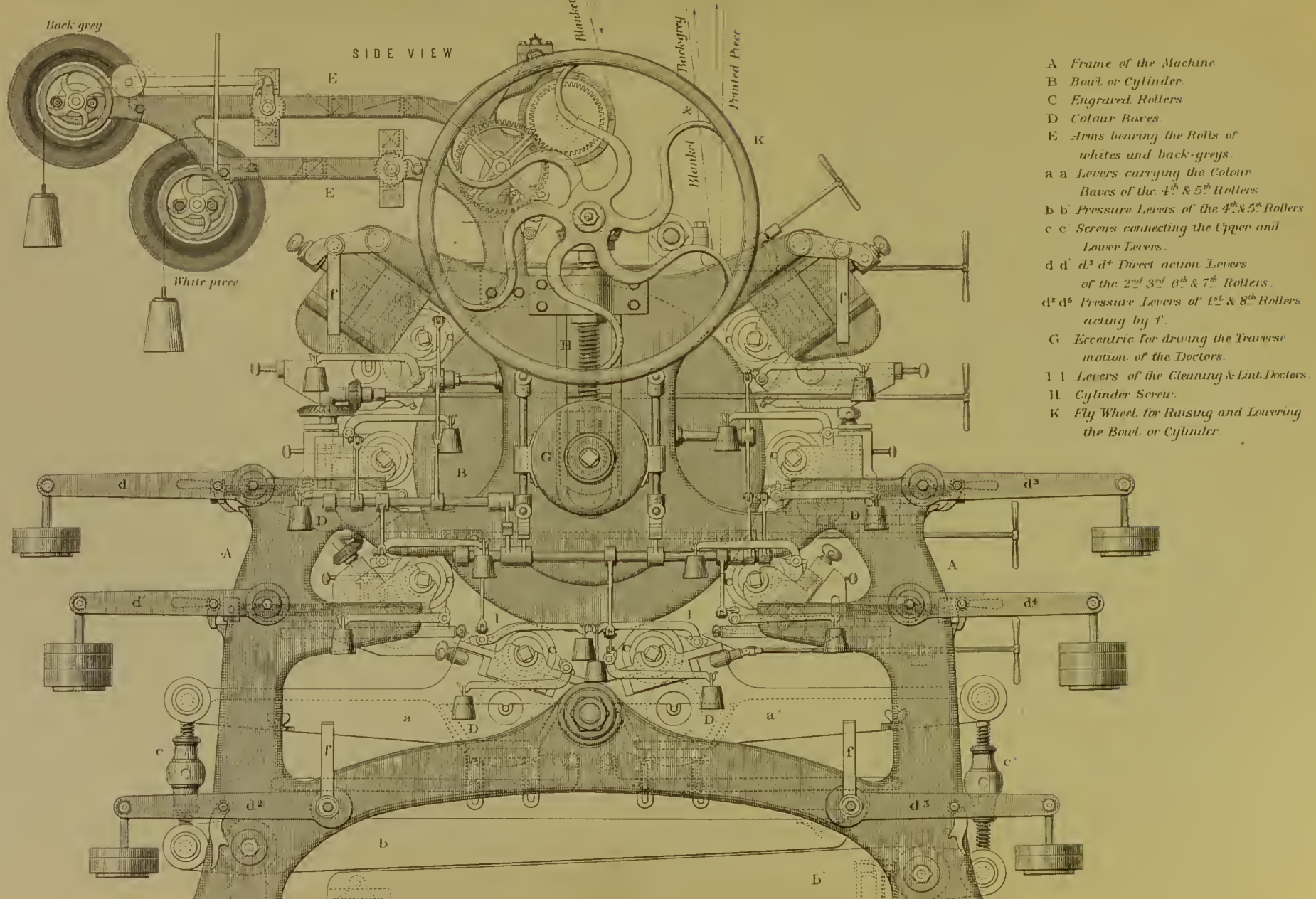
FRONT VIEW

A *Bowl or Cylinder.*
B *Engraved Roller.*
C *Colour Box.*
D D *Scrimp Roller.*
E *Eccentric to drive traverse motion.*
F *Fly Wheel for Raising & Lowering Bowl.*
G *Blanket Roller.*
H *Double Cylinder Oblique Engine to drive Machine.*




WILLIAM MACKENZIE, LONDON, EDINBURGH & GLASGOW

# EIGHT COLOUR PRINTING MACHINE BY TULPIN FRERES



fusion with caustic potash this forms potassium sulphate and reproduces alizarin, and does not (as might have been expected) give rise to potassium sulphite and an oxy-alizarin.

The conversion of anthracene into alizarin may be accomplished in several ways, in some of which anthracene is not itself used as an intermediate product. These methods may be summarized as follows:—

(A.) Original process patented by GRŒBE and LIEBERMANN in 1868. Anthracene is first converted into anthraquinone by either of the following processes:—(1.) Treatment of 1 part anthracene with 2 of potassium dichromate and sulphuric acid, with or without the addition of strong acetic acid. (2.) Oxidation of anthracene by dichromate, both dissolved in glacial acetic acid. (3.) Oxidation by nitric acid of medium strength, acetic acid being also added.

The anthraquinone thus obtained is purified and converted into *dibromanthraquinone* by treatment with 4 equivalents of bromine in closed vessels at 80° to 130° C. thus—

Anthraquinone. Dibromanthraquinone.

$$C_{14}H_8O_2 + 2Br_2 = C_{14}H_6Br_2O_2 + 2HBr.$$

The resulting dibromanthraquinone is then heated to between 180° and 260° C. with a concentrated solution of caustic soda or potash in closed vessels, when the following reaction takes place, potassium alizarate being formed, from which alizarin is produced by the action of acids.

Dibromanthraquinone. Potassium hydrate. Potassium bromide. Potassium alizarate.

$$C_{14}H_6Br_2O_2 + 4KOH = 2KBr + C_{14}H_6O_2(OK)_2 + 2H_2O.$$

Potassium alizarate. Hydrochloric acid. Potassium chloride. Alizarin.

$$C_{14}H_6O_2(OK)_2 + 2HCl = 2KCl + C_{14}H_6O_2(OH)_2.$$

The "melt" is dissolved in water, and hydrochloric or sulphuric acid added, upon which the alizarin is thrown down in flakes, which are collected, washed, and drained, and sent into the market as a paste.

In the same way dichloranthracene may be prepared from anthracene and chlorine, and converted into alizarin.

In a subsequent patent GRŒBE and LIEBERMANN avoid the necessity of producing anthraquinone, by treating anthracene itself with 8 equivalents of bromine, when dibromanthracene tetrabromide is formed—

Anthracene. Dibromanthracene tetrabromide.

$$C_{14}H_{10} + 4Br_2 = 2HBr + C_{14}H_8Br_2,Br_4.$$

The product is then heated with alcoholic potash, and is converted into tetrabromanthracene.

Dibromanthracene tetrabromide. Tetrabromanthracene.

$$C_{14}H_8Br_6 = 2HBr + C_{14}H_6Br_4.$$

By the action on this of 5 parts of slightly dilute nitric acid at 100° C. dibromanthraquinone is formed and bromine set free:—

Tetrabromanthracene. Dibromanthraquinone.

$$C_{14}H_6Br_4 + O_2 = C_{14}H_6Br_2O_2 + Br_2.$$

This dibromanthraquinone is then converted into alizarin as before. Chlorine may be substituted for bromine in this case also.

(B.) Process patented by BRŒNNER and GUTZKOW. Anthracene is converted into anthraquinone by nitric acid of sp. gr. 1·3 to 1·5, and the product purified; the anthraquinone is then heated with sulphuric acid, and mercuric nitrate added. The product of the action is dissolved in a caustic alkaline solution, filtered, and saturated with an acid; a precipitate containing both alizarin and purpurine (anthrapurpurine) being thrown down. Although this patent is not clearly worded, yet it points out that sulphonic acid can be used in lieu of bromine, and hence is really the foundation of the more recent processes for the manufacture of artificial alizarin (C). The mercuric nitrate oxidizes the anthracene disulphonic acid first formed to anthraquinone disulphonic acid, and then becomes converted into alizarin by the alkali. To obtain a profitable amount of product, however, excess of alkali must be used, the whole evaporated to dryness, and the residue fused, an operation not mentioned in the patent specification.

(C.) In June, 1869, GRŒBE, LIEBERMANN, and CARO patented the following process:—Anthraquinone is heated with sulphuric acid, whereby anthraquinone disulphonic acid is formed. Excess of sulphuric acid is then removed by means of chalk, sodium carbonate added, and the resulting sodium anthraquinone disulphonate fused with 2 to 3 parts caustic soda, producing alizarin thus:—

Anthraquinone disulphonic acid. Sodium hydrate. Sodium sulphate. Alizarin.

$$C_{14}H_6O_2(HSO_3)_2 + 4Na(OH) = 2Na_2SO_3 + 2H_2O + C_{14}H_6O_2(OH)_2.$$

This patent was dated June 25 (England). On the next day W. H. PERKIN took out a patent for nearly the same process. This chemist also observed that oxyanthraquinone monosulphonic acid is formed, $C_{14}H_6O_2\begin{cases}SO_3H,\\OH\end{cases}$ as an intermediate product between the disulphonic acid and alizarin. This gives the blue cast to the "melt." Perkin has also patented the production of anthraquinone disulphonic acid by the oxidation of the chloro- and bromo-sulphonic acids formed by acting with sulphuric acid on chlorinated and brominated anthracene.

(D.) In a subsequent patent GRŒBE, LIEBERMANN, and CARO obtain anthraquinone disulphonic acid, without the previous preparation of anthraquinone, by treating anthracene with sulphuric acid, and oxidizing the resulting anthracene disulphonic acid with manganese dioxide or some other oxidizing substance.

Anthracene disulphonic acid. Anthraquinone disulphonic acid.

$$2C_{14}H_8(HSO_3)_2 + 3O_2 = 2C_{14}H_6O_2(HSO_3)_2 + 2H_2O.$$

To prepare the anthraquinone disulphonic acid in this way, 1 part of anthracene and 4 of strong sulphuric acid are heated to 100° C. for about three hours, the temperature being then raised to 150° C. or upwards for another hour or more. Three parts of water are added to the product after cooling,

when unaltered anthracene is precipitated, which is collected and used over again. The acid filtrate is heated to boiling, and 3 parts of powdered manganese dioxide added gradually. The whole may be advantageously evaporated to dryness and heated for some time. The resulting mass is dissolved in boiling water. Milk of lime is added till alkaline and manganous oxide are thrown down. The solution of calcium anthraquinone disulphonate thus produced is strained off from gypsum, &c. (the solid mass being washed and pressed), and decomposed by sodium carbonate. The filtered solution of sodium salt is evaporated to dryness and fused with caustic soda.

(E.) On January 24, 1870, DALE and SCHORLEMMER patented the following process:—Anthracene is *boiled* with 4 to 10 parts of strong sulphuric acid (the action consequently takes places at a higher temperature than in the preceding method). The product is converted into a barium, calcium, potassium, or sodium salt, which is purified by re-crystallization. To a solution of one of these salts excess of caustic soda or potash, and a quantity of nitrate or chlorate of potassium equal to the weight of anthracene, is added. The whole is then evaporated to dryness, and heated to 180° to 260° C., when a blue violet colour appears. From the "melt" alizarin is extracted by solution in water, and addition of a mineral acid in the usual way. In this case the anthracene disulphonate becomes oxidized to anthraquinone disulphonate by the nitrate or chlorate, and the product is converted into alizarin by the caustic alkali.

(F.) MEISTER LUCIUS and BRUNING prepare anthraquinone by oxidizing anthracene with a mixture of nitric acid and potassium dichromate. From this nitro-anthraquinone is formed by the action of nitric acid. On treatment with alkali alizarin is produced, mixed with a little purpurin (anthrapurpuriu.)

(G.) GIRARD prepares impure tetrachloranthracene by acting on anthracene with a mixture of hydrochloric acid and potassium chlorate. This is oxidized by nitric acid or by red oxide of lead, and either sulphuric or acetic acid. Dichloranthraquinone and chloroxanthranyl chloride result. The mixture is then treated with oxide of zinc, lead, or copper, and alcoholic sodium acetate, when alizarin is formed. The alizarin thus produced may be purified by treatment with benzol, petroleum distillates, or other solvents by which the foreign matters can be dissolved out; or the alizarin may be dissolved in an alkaline solution, and reprecipitated (after filtration) by an acid, the process being repeated several times.

The preparation of alizarin by any of these processes is a matter of some delicacy. If too high a temperature be attained, the alizarin already formed is more or less destroyed, benzoic acid and other products being formed; whilst the anthraquinone disulphonic acid is more or less converted back again to anthraquinone, or even into anthracene. In the processes by which anthraquinone disulphonic acid is formed, if the heating be not continued long enough, or if the temperature be not high enough, considerable loss is occasioned by the formation of the intermediate oxyanthraquinone sulphonic acid. In process (E), if too much nitrate or chlorate be used, the alizarin is apt to be further acted on and destroyed; whilst if too little be employed, then loss is occasioned by incomplete oxidation. Under certain not well understood circumstances anthraquinone mono-sulphonic acid is formed during the melting, from which results oxyanthraquinone instead of alizarin. The same substance is formed if anthracene mono-sulphonic acid has been formed through the incomplete action of sulphuric acid on anthracene in processes (D) and (E), or if anthraquinone mono-sulphonic acid has been produced through the incomplete action of sulphuric acid on anthraquinone in process (C).

*Manufacture of Alizarin.* — The method first used in England was that which is now called the anthraquinone process; but owing to the great difficulty in obtaining sufficiently pure anthracene, after a few trials it was abandoned in favour of the chloranthracene process, which was found to give much better results.

The anthracene used for the manufacture of alizarin by the latter process is chiefly obtained from the dead oils of coal tar; an inferior kind is produced from the distillation of pitch, but is not well adapted to the purpose on account of the difficulty in removing the higher series of hydrocarbons. The dead oils from different coals vary considerably in the amount of anthracene they yield. Those obtained from coal in the neighbourhood of Staffordshire contain the most, and the Scotch coals the least. In the fractional distillation of the dead oils a large amount of naphthalene is deposited in the first portions, the anthracene occurring more abundantly towards the middle of the operation; towards the end the anthracene becomes more or less contaminated with the higher series of hydrocarbons, according to the degree the distillation is pushed. Only practice will enable the operator to determine at what point it is best to collect the anthracene, both the first and latter portions of the distillate being returned to the still for further fractionating.

On cooling, those portions of the oil which have been set aside deposit the anthracene as a sandy precipitate of a green colour. When the tanks are cold, or nearly so, the anthracene is scraped off the sides of the tank, and the oils loaded with the deposited anthracene are filtered through canvas bags hung over open tanks, into which the oils drain and are stored for further distillation. After sufficient draining the bags are detached from the frames in which they hung, and folded for the hydraulic press. After pressure has been applied the bags are taken out, and the anthracene appears in the form of a hard greenish cake.

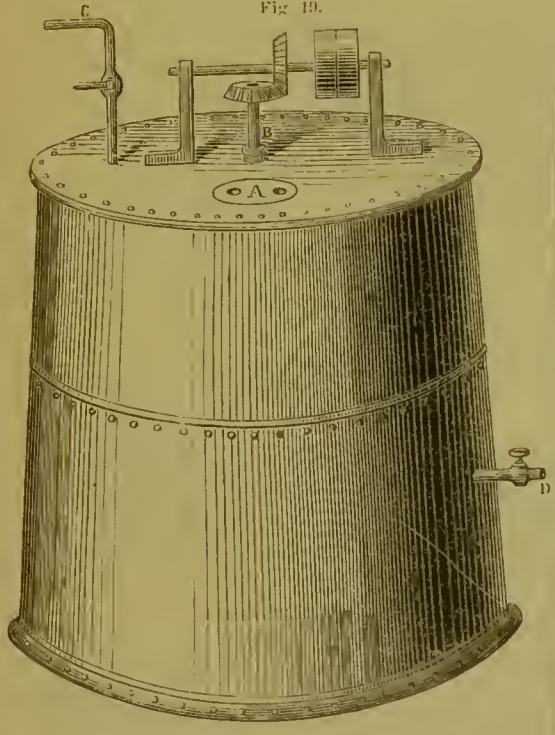
Some tar distillers remove a further portion of the oily impurities by hot pressure. This method of purification is not much in vogue, however, on account of the solubility of the anthracene itself in its own impurities at an elevated temperature.

As the anthracene prepared with or without hot pressure is much too impure to be used for the production of colour, it is necessary that the solid

impurities (*e.g.*, naphthalene, phenanthrene) be got rid off by washing with oils or naphtha. This purification is accomplished in the following manner.

The cakes of crude anthracene are first crushed under edge-runners, and ground into a thick paste. This paste is then removed in boxes and drawn up to the top of the building, and transferred from thence into a large jacketed vessel (Fig. 19) of wrought iron of cylindrical form, and about 6 feet

Fig. 19.




high and 5 in diameter. This vessel is closed with the exception of a door on the top, A, by which the anthracene paste is admitted, and is provided with an iron stirrer, B, which passes through a stuffing box and is driven by machinery. The apparatus having been about half filled with American light oils by the oil cock, C, the paste is then stirred in, a little steam being admitted within the jacket to assist the incorporation. When the oil boils the contents are run out into tanks to cool for one or two days.

After cooling the tanks are stirred up and the thick liquid is run into a large iron tank, containing a false bottom of wood pierced with holes, and covered with canvas, through which the oils laden with the soluble impurities of the anthracene percolate, running off into a large closed receiver placed underneath the filter.

The oils thus filtered are pumped from the receiver into a large still heated by steam. The oils are distilled off and are condensed in a leaden worm attached to the still, and run into a receiver on the ground floor. The impurities are then run off into a separate tank, and on cooling become solid.

The anthracene remaining on the filter is then raked out from manholes in the sides, and placed in a still, the adhering oils being driven off by a current of steam.

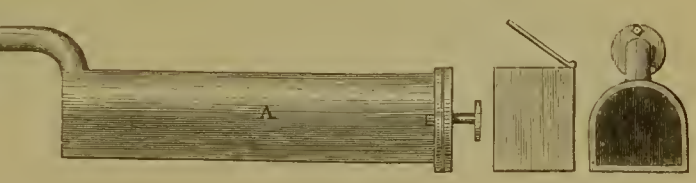
In this state the anthracene presents the appearance of a blackish green powder; but before submitting it to the action of chlorine, it is necessary to remove certain impurities which would interfere with the production of good crystals of chloranthracene. In order to accomplish this the anthracene is distilled with from 15 to 20 per cent. of caustic potash, soda not being found to answer the purpose. The distillation is conducted in gas retorts (Fig. 20), which may be set in benches of three. The potash broken in small pieces is ground under edge-runners with the anthracene. The necks of the retorts, A, are connected with long sheet-iron receivers, B, provided with loosely fitted lids, so that the gases evolved during the distillation may have free vent in case of their taking fire from the overheating of the retorts. Sections of a retort and receiver are shown in Fig. 21.

The retorts being charged with about 2 cwts. of the mixture, are then heated by the furnace, and at a heat short of redness the anthracene distils over and condenses in the receivers, partly in the form of a crystalline cake, and partly in a light sublimate of a pale yellow colour. The impurities are left in the retort combined with the potash as a porous black mass, which after removal readily takes fire on exposure to the air, and continues to burn until all the carbon is consumed, leaving the potash in the

Fig. 20.




Fig. 21.

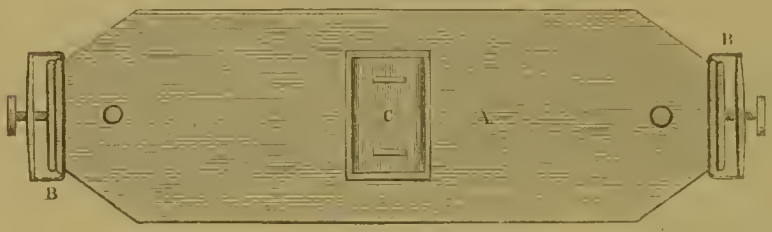



form of carbonate, which is reconverted into caustic potash for use in subsequent operations. The anthracene thus obtained is ground under edge-runners and placed in wooden trays, which are arranged on shelves in a drying room.

When perfectly dry it is ready to be submitted to the action of chlorine, and for that purpose it is placed in about 3 cwt. charges in an oblong leaden receptacle, A (Fig. 22), 10 feet in length, 5 in breadth, and about 18 inches deep, supported by woodwork. At each end of the apparatus a door, B B, is fixed with a screw and crossbar, in the manner of a gas retort lid. The anthracene is introduced by an aperture, C C, on the top of the vessel, which is closed by a leaden cover, the sides of which dip into a channel formed round the opening, filled with dead oils in the manner

of a water lute, see section Fig. 23, which also serves as a safety valve in the case of the chlorine being admitted too rapidly. The apparatus is supported by iron plates, under which steam is admitted in order to assist the reaction. The chlorine is admitted from either end of the apparatus, and after traversing the vessel the hydrochloric acid gas and excess of chlorine are conducted by a leaden pipe from the other end into

Fig. 22.



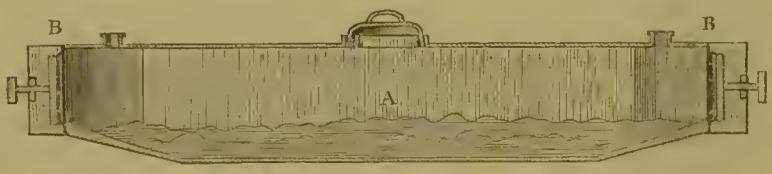
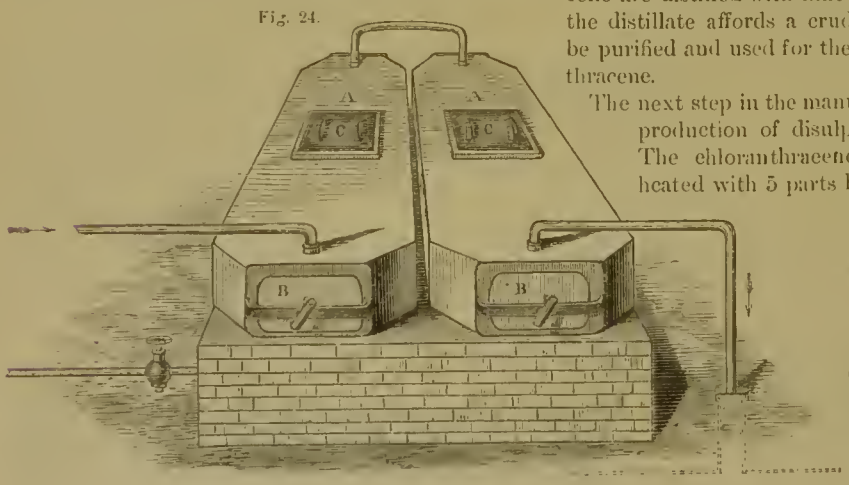




Fig. 23.

another similar vessel also filled with anthracene, which readily takes up the excess of chlorine. The hydrochloric acid gas is then conducted into a flue connected with a scrubber filled with coke and supplied with water, which condenses the gas, the acid thus condensed being used for the elimination of chlorine. As soon as the anthracene in the first vessel has been entirely converted into chloranthracene, the product is raked out from the doors at each end into wooden tubs; and a fresh charge having been introduced, the leaden pipes which conduct the chlorine are reversed, the chlorine being passed over the second vessel. The excess of chlorine and hydrochloric acid gas, after traversing the first vessel containing the new charge, escapes as before into the flues connected with the scrubber. A sketch showing the two vessels connected is given in Fig. 24, the wooden supports and a portion of the brickwork being removed for clearness.

Fig. 24.




In the production of chloranthracene it is necessary that the anthracene oil used in the operation should not contain more than 50 per cent. of pure anthracene, as the impurities associated with it are necessary for its solution whilst absorbing the chlorine. If purer anthracene were employed only a partial combination would be effected, as the anthracene remaining undissolved would only be superficially attacked.

When removed from the apparatus the chloranthracene presents the appearance of a black sludge, and hardens on cooling. The hydrochloric acid associated with it is neutralized by a solution of caustic soda; and when heated by steam the semi-fluid mass is ladled out into bags, which are submitted to hydraulic pressure whilst hot, until the oils are as far as possible removed. The chloranthracene then appears as brownish-yellow crystalline cake. This is further purified by breaking it up and mixing it with naphtha, pressing it, and repeating the operation once or twice, until the substance has assumed the appearance of a golden yellow friable cake: it is then crumbled up and dried. This should contain from 80 to 90 per cent. of pure chloranthracene.

The oils which exude from the crude chloranthracene are distilled with lime in cast-iron retorts; and the distillate affords a crude anthracene which may be purified and used for the manufacture of chloranthracene.

The next step in the manufacture of alizarin is the production of disulpho-anthraquinonic acid. The chloranthracene, purified as above, is heated with 5 parts by weight of oil of vitriol in cast-iron pots (Fig. 25) to a temperature of 160° C. for an hour. The cast-iron pots employed, A, are about 2 feet wide and 2½ feet deep; they are cast half-closed at the top, the remaining half being covered by a semi-circular sheet of thick lead, Fig. 26, having a small opening to admit of the introduction of the chloranthracene, about 1 cwt. of chloranthracene forming the charge. The gases evolved during the reaction are conveyed to a scrubber by means of stoneware pipes fixed in a socket, B, cast on the top of the pot. (Three pots thus connected are shown in Fig. 27.) A small quantity of anthraquinone sublimes into these pipes, which is at times scraped out, washed, dried, and then

mixed with the chloranthracene for use in other operations.

Great care must be taken to see first that the chloranthracene be sufficiently pure and dry, and also that the oil of vitriol is at its maximum strength, otherwise loss will result from the boiling over of the pots, and the formation of other products than disulpho-anthraquinonic acid. After the heat has been raised to 160° C. for about an hour, the vessel and contents are allowed to cool somewhat; and while still fluid and having the appearance of coal tar, it is ladled out into copper pails, the contents of which are poured into large rounds, fitted with wooden stirrers, holding about 1000 gallons. These rounds are half-filled with water and the washings of filters. Slaked lime is added till the liquor is neutral to test paper, and steam being introduced the liquid is, whilst being continuously stirred, brought to the boil, upon which a plug having been withdrawn, the thick liquid is run by means of wooden shoots on to the filters placed beneath the rounds.

The filters are formed with 3-inch deals, and are about 12 feet square and 2½ feet in depth. The bottom is covered with a layer of smooth bricks, supported by bricks placed edgeways and arranged in channels, so as to afford a free exit for the filtered liquor. Small pebbles, about the size of peas, are scattered over the bricks to the depth of about 1 inch, and over these a layer of sand 2 inches in thickness is spread. A coarse jute canvas is then thrown over the sand, which is secured in its place by slight wooden frames, the edges of the canvas being tacked to the sides of the filter.

At the centre, underneath the filter, is fixed a wrought-iron pipe to carry off the liquor. This pipe is connected with a cylindrical receiver of wrought iron, capable of containing about 1000 gallons, and exhausted by means of an air-pump. A second receiver is also connected with each filter, in order that whilst one is being emptied the other may be filling. A glass gauge is affixed to each receiver to indicate the state of the contents. When the

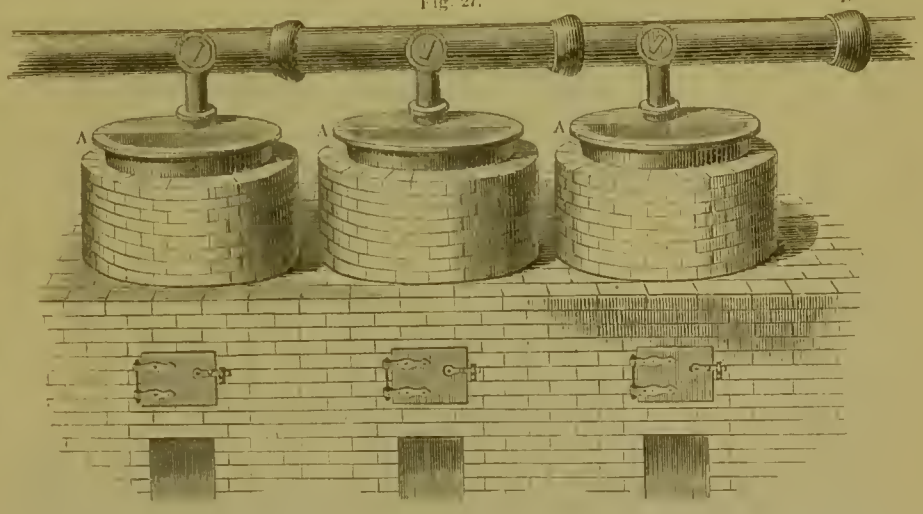
Fig. 25.






Fig. 26.

Fig. 27.




receiver is full the vacuum is shut off, and air being admitted by a cock on the top of the apparatus, the liquor is run out into semicircular evaporating pans, which are from 20 to 30 feet long and 7 or 8 feet wide. These pans are formed of half-inch iron plates, flush-rivetted on the inside and jacketed outside, and are connected with the steam main. They are coated on the outside with felt and set in brickwork. Their tops are covered with wood-work, in the centre of which rises a wooden chimney carried through the roof of the building, by which the steam escapes into the air.

After the liquor from the receivers has run off into the pans the black mud left on the filter is taken up and boiled in the rounds with the weak washings of former operations. The liquid is filtered through the vacuum filters, and the filtrate is conducted into the receivers which contained the first liquors, the weak liquors being evaporated with the strong. The residue is again taken up into the rounds and boiled with water, the liquid as before being run into the filters, the weak liquors being conducted to receivers appropriated to them, of similar form and size to those already described. The operation of boiling the residues with water is repeated once or twice until the soluble calcic di-sulphanthraquinonate is washed out, the weak liquors being used as above. The liquors containing the calcic di-sulphanthraquinonate are then evaporated to about one-third of their volume, when sufficient soda crystals are added to precipitate the lime as carbonate, the sodium salt remaining in solution. When the calcium carbonate has settled the liquor is drawn off and evaporated in another pan of similar construction, until the liquid contains about 25 per cent. of dry sodium di-sulphanthraquinonate. The solution is then drawn off and stored in open cast-iron tanks, provided with a stopcock for the purpose of drawing off the contents when required.

The next operation of the manufacturer is the conversion of this salt into sodium alizarate.

About 6 cwts. of the liquor is put into a jacketed iron vessel heated by steam, and to this is added

3 cwts. of caustic soda, previously dissolved in a small quantity of water; the bulk is then made up to about 150 gallons. During the mixing the liquid thickens, and in that state is run into a strong wrought-iron vessel (Fig. 28) capable of bearing a pressure of 300 lbs. per square inch. Fig. 28 shows a drawing of the apparatus, which consists of ten upright tubes connected with a large horizontal tube:—A, pipe for discharging the contents of the tube; B, pipe used in charging the apparatus; C, stop valve closed during operation; D, cock for letting off superfluous steam; E, cock connected with the steam main. The front of the apparatus, showing the door, F, for cleaning out, is represented in Fig. 29. The mixture is heated in this vessel, which is set in an oven heated by flues to a temperature of about 160° Centigrade, a thermometer and pressure-gauge being used to regulate the temperature. This heat is continued from eight to twelve hours or more, the best result being obtained when the temperature is low and long continued. It is also advantageous to introduce a small quantity of chlorate of potash into the mixture before heating, as a reduction occurs occasionally within the vessel, anthraquinone or even anthracene being formed. In an early stage of this operation an intermediate product is formed, which becomes converted into alizarin by continued heating with the alkali. Samples are taken out at times, which are dissolved in water, and the alizarin precipitated by an acid. The filtered liquor is then rendered alkaline by potash or soda, and according to the diminution of the violet colour produced the finish of the operation is determined. The conversion being completed, a cock connected with the apparatus is opened, and the product is then forced by the pressure of the steam within the pan into an iron tank placed on the top floor of the building. As soon as the thick liquid is thus expelled the surplus steam is allowed to

Fig. 28.

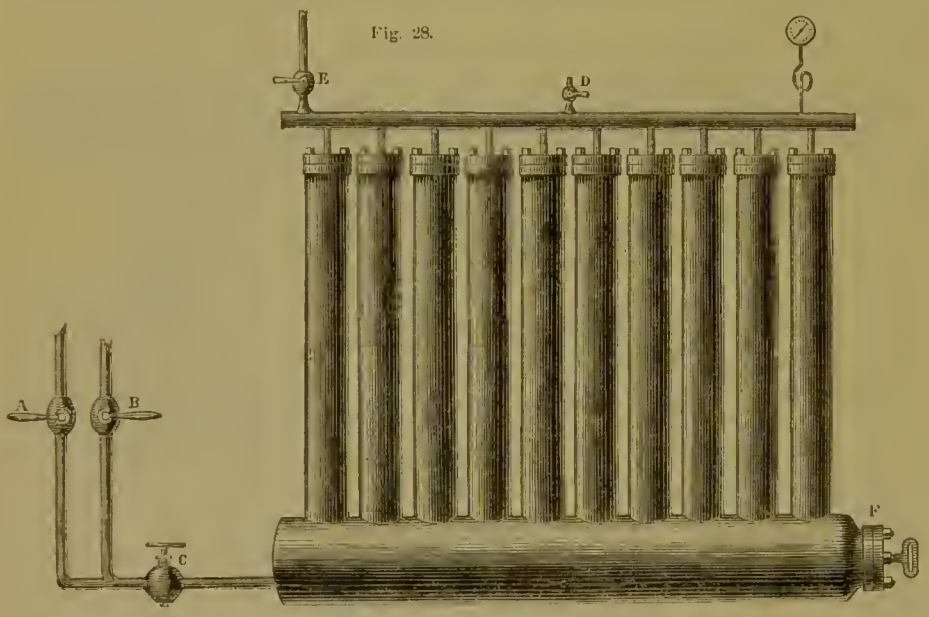



Fig. 29.



escape by opening a cock on the top of the apparatus. Boiling water is then admitted into the vessel, which dissolves all that may have adhered to the sides, and the steam being admitted, the washings are forced up into the tank containing the colour, which prevent the liquid from setting before it is precipitated. On the floor below this tank are placed wooden backs lined with lead, which are used for precipitating the alizarin from its alkaline solution. These tanks are half filled with dilute sulphuric acid, and while still hot the alkaline liquor is slowly added until the acid is completely neutralized, which is known by the alteration of colour which ensues as soon as an excess of the alkaline solution is added. During the precipitation large quantities of sulphurous acid gas are generated, which are conveyed by wooden flues into the open air. The liquid is continually stirred during the operation to prevent the tanks from frothing over. When the precipitation is complete the liquid presents a bright yellow colour, due to the particles of alizarin, which after standing a few hours settle down. The supernatant liquor having been drawn off, the tanks are filled up with water, and well boiled by means of a steam-pipe until the precipitate becomes more dense and easy to filter. The filters used for the alizarin are nearly of the same description as those used to filter off the calcium di-sulphanthraquinonate. They are provided with covers to prevent the introduction of dust, and calico is used in the place of the coarse canvas. A cleaner kind of filter without bricks is also used, which is constructed in the following manner:—Several lengths of wood 2 inches square, notched at intervals on the under side to allow of the free escape of the liquor, are placed on the floor of the filter at distances of about 1 foot apart. Over these is laid a flooring of inch boards pierced with numerous small holes, and over the flooring is stretched a piece of thick felt, such as is used for carpets; over the felt a sheet of calico is tacked to the sides of the filter, and secured in its place by slight wooden frames. These filters are connected

with an exhausted receiver in the same manner as those with brick bottoms.

The clear liquors being drawn through, the alizarin lying on the filters is washed with hot water, applied by an india-rubber hose, having a rose jet at its extremity, until all the soluble salts are removed. The liquors run from the receiver into a large tank lined with lead and there deposit any alizarin the hot water may have dissolved, which is afterwards collected and purified. When sufficiently washed the alizarin, now of a bright orange yellow colour, is removed from the filters into large oaken rounds, and well agitated, until it becomes a thick liquid. A sample is then taken out and tested for strength and colour in the following manner.

Ten grammes of the colour to be tested are shaken up with water, and made up to 400 cubic centimètres. 10 grammes of the standard colour are also made up to the same volume. Some glass beakers, each containing an equal quantity of distilled water, are placed in a copper water bath half filled with water. To these beakers are added different portions of the colour to be tested, one of the beakers being reserved for the standard colour, 10 cc. of which are introduced therein. A number of pieces of cloth mordanted in stripes with alumina and iron, and combinations of these two, are soaked in water, and a piece of equal size placed in each beaker. The vessel is then heated gradually over a gas lamp or sand bath for about an hour, until it comes to the boil, the pieces of cloth being well stirred during the heating. After the boiling point is reached, this temperature is kept up for about one half hour more, when the pieces of cloth are removed from the beakers, and well washed in distilled water. They are then soaped in a solution containing ½ oz. of soap to the gallon of distilled water, and in a few minutes are taken out, well washed, and dried. The pieces are then compared with the standard, and the quantity of water necessary to bring the colour to standard strength is found by calculation. After the addition of the water the colour is stirred well for about an hour, and is then ready to be drawn off into casks for use.

Although usually styled alizarin, the colour made by this process consists mainly of anthrapurpurin, with an admixture of only a small proportion of alizarin. It produces a much more orange shade with alumina mordants than alizarin, and is on that account much used for Turkey red dyeing. A much larger quantity of alizarin may be produced in the colour if only two parts of sulphuric acid are used in the place of four or five. As yet, however, this has not been done, on account of the loss which takes place during the combination, before the requisite temperature for the formation of a mon-acid anthraquinone is produced.

The progress of the operation during the melting may be judged by taking out samples from time to time, dissolving in water, adding sulphuric acid, and noticing the quantity of flakes thrown down. At first these are few, but as the action goes on the alizarin is formed, and the precipitate becomes larger.

Alizarin may be distinguished from oxyanthraquinone monosulphonic acid by its solubility in ether, the latter remaining undissolved when the liquid and precipitate are agitated with ether in a test tube. The crude alizarin precipitated by acids from the solution of the "melt" usually requires some purification before it is fit for use in dyeing. By washing with water, adhering acid, alkaline salts, &c., are removed, and also some of the oxyanthraquinone monosulphonic acid. Oxyanthraquinone and anthraquinone, however, are apt to be present, and to remove these the product is dissolved in dilute caustic soda ley (free from alumina, otherwise loss ensues from the production of alumina lake). After standing some hours the clear portion is run off, the last portions being filtered, and dilute sulphuric acid is then added in slight excess, so as to precipitate a purified alizarin. A better method is to add calcium chloride solution to the caustic soda alizarin solution, a calcium alizarin lake being thrown down, whilst oxyanthraquinone mostly remains in solution. The filtered and washed lake is then decomposed by hydrochloric acid, forming calcium chloride, alizarin being regenerated.

AUERBACH purifies alizarin by dissolving the crude material in caustic soda, filtering, and passing carbon dioxide into the liquor. A mixture of alizarin and sodium alizarate is precipitated. This is then collected, washed, and treated with hydrochloric acid.

The precipitated alizarin is then washed on calico filters till the runnings are no longer acid, and allowed to drain thoroughly. The thick mass is then placed in a closed copper rotating drum, containing a stone or copper ball; the alizarin thus becomes very finely divided, the whole being converted into a thick paste, which has but little tendency to subsidence, an inconvenient phenomenon often exhibited by the crude product, and leading to want of uniformity in composition of the contents of each keg of paste made. This paste is then packed for the market in glass jars, wooden kegs, or zinc boxes. It usually contains 10 to 15 per cent. of dry alizarin. The shade varies slightly, some varieties having a yellow cast, which renders them more suitable for scarlets, others possessing a violet or lilac shade.

Simultaneously with artificial alizarin at least three other allied products are formed, viz:—

| | |
|---|---|
| Oxyanthraquinone, | $C_{14}H_7O_2(OH)$. |
| Anthraflavic acid (PERKIN), | $C_{14}H_6O_2(OH)_2$. |
| Anthrapurpurin (PERKIN), isopurpurin (AUERBACH), | $C_{14}H_5O_2(OH)_3$. |

The first of these products is probably formed from mono-substitution compounds of anthraquinone, produced during the manufacturing process. The second, as PERKIN has shown, is isomeric with alizarin. The third body was supposed for some time to be identical with the purpurin of madder; but PERKIN has recently shown that it is only isomeric therewith. AUERBACH has also come to the same conclusion from his experiments.

A colouring matter of an orange tint has been prepared from anthracene; this is also an anthraquinone derivative, being diamido-anthraquinone,

$C_{14}H_6(NH_2)_2O_2$. Bœttger prepares this substance by acting on dinitro anthraquinone with reducing agents, such as sodium stannite, sodium or ammonium sulphydrate, sodium sulphide, &c., the action being analogous to that by which aniline is formed from nitrobenzol (*vide* article Aniline),

$$C_{14}H_6(NO_2)_2O_2 + 6H_2 = 4H_2O + C_{14}H_6(NH_2)_2O_2.$$

From experiments made by Auerbach, Bœttger, and Petersen, it seems very probable that this body may ultimately turn out to be the parent of a number of other dyestuffs.

Springmuhl has extracted a blue colouring matter from the bye products of the manufacture of alizarin; as yet, however, this substance has not been subjected to much study, and has no commercial importance.

**COBALT.**—*Cobalt*, French; *kobalt*, German. Symbol Co. Atomic weight, 58·8; atomicity, 2, 3, and 6.

*History.*—This metal was not known until within comparatively recent times. It had been supposed, from the beautiful blue colour of specimens of ancient glass and enamel, such as the tiles of some Roman tesselated pavements, that it was known in very early times; but as cobalt has never been found in any of these, and since it has also been shown by Gmelin that a beautiful blue colour may be produced in glass by the presence of oxide of iron or oxide of copper (as, for example, the resplendent colours of many iron and glass-house slags), it appears most improbable that the ancients were acquainted, even empirically, with the property of cobalt to impart a blue colour to glass, or that they ever used any cobalt mineral for that purpose.

The Bohemian and Saxon miners, about the fourteenth or fifteenth century, seem to have been often disappointed in their efforts to obtain copper and other metals useful to them, finding in their stead a mineral then useless, and which often deluded them with the hope of valuable ore. They gave to the mineral the name of *kobalt*, comparing it to Kobalus, a supposed malicious sprite, which in their superstition they supposed to haunt the mines and destroy their works, giving them much annoyance; it appears even to have been customary to introduce into the church service a prayer for the protection of the miners from "*kobalts* and spirits."

In course of time it was discovered that this mineral imparted a fine blue colour to glass; and after having been used for this purpose for more than two centuries, it in 1733 attracted the attention of the celebrated Swedish chemist, Brandt, who obtained from it a new "semi-metal," as he described it, to which he gave the name of *cobalt*.

Lehmann in 1761 wrote a very complete account of this body, and the discovery of Brandt was subsequently confirmed by Bergman about 1780. It has since been examined by Tessaert (Ann. de Chim. xxviii. 101), by Thénard (ibid. xlii. 210), and by Prout (ibid. lx. 260).

*Natural History.*—Cobalt occurs in nature usually in association with the ores of nickel, copper, and bismuth, and also occasionally with manganese. It is found in the metallic state in some specimens of meteoric iron, varying in quantity from 2 to 0·6 per cent.

The following are the most important minerals:—

*Smaltine.*—Arsenical cobalt or tin white cobalt is one of the most plentiful of the cobalt minerals, and occurs chiefly associated with the ores of bismuth, nickel, and copper, at Schneeberg in Saxony, at Joachimsthal in Bohemia, and at Wittichen, Siegen, Saalfeld, and Mansfeld. It is the most frequently-occurring English mineral, and is found in this country at Huel Sparnon, near Redruth, and also at Dolcoath and Herland, all in Cornwall.

It is of a tin-white colour, inclining when massive to steel-grey, and occurs in crystals of the cubic system, which are frequently fissured in all directions, and also in reticulated, botryoidal, stalactitic, and amorphous forms. At Riechelsdorf, in Hesse, its veins are inclosed in cupriferous shale, and the net-like variety from Joachimsthal is frequently imbedded in calcareous spar.

Its composition is that of cobalt arsenide, $CoAs_2$, in which, however, the cobalt is often more or less replaced by iron, nickel, and copper. The following analyses are by Stromeyer (*a*) and by Varrentrap (*b*):—

| | (*a*) Riechelsdorf. | (*b*) Tunaberg. |
|---|---|---|
| Cobalt, | 20·31 per cent. | 23·44 per cent. |
| Arsenic, | 74·21 " | 69·46 " |
| Iron, | 3·42 " | 4·95 " |
| Copper, | ·15 " | — " |
| Sulphur, | ·88 " | ·90 " |

Before the blow-pipe it emits copious arsenical fumes, and gives a blue bead with borax or microcosmic salt. It may be distinguished from cobaltine by the absence of any distinct cleavage. It dissolves in nitric acid, usually giving a pink solution.

*Cobaltine.*—Cobalt glance, or bright white cobalt, is the next, and perhaps the most important mineral, since it is this that forms the bulk of the cobalt ores of commerce.

It is met with, in large distinctly-pronounced crystals belonging to the cubic system, at Tunaberg and Hakansbö, in Sweden, and at Skutterud in Norway. It occurs abundantly in mica slate at Wehna in Sweden, less frequently at Querbach in Silesia, and also in the vicinity of St. Just and St. Austell in Cornwall. It may be distinguished from smaltine by its inferior specific gravity and reddish hue; also by its lamellar structure, its more distinct cleavage, and by its requiring considerably greater heat to drive off the arsenic. The colour is silver or yellowish-white, tinged with red.

Its composition is that of a combined arsenide and sulphide of cobalt, CoAsS. The following are analyses of it by Stromeyer (*a*) and Klaproth (*b* and *c*):—

| | (*a*) Skutterud. | (*b*) Tunaberg. | (*c*) Tunaberg. |
|---|---|---|---|
| | Per Cent. | Per Cent. | Per Cent. |
| Cobalt, | 33·10 | 36·66 | 41·00 |
| Arsenic, | 43·47 | 49·00 | 55·00 |
| Sulphur, | 20·08 | 6·66 | ·50 |
| Iron, | 3·23 | 5·66 | — |
| Deficiency, | ·12 | 2·02 | ·50 |

*Erythrite*, or *Cobalt Bloom*, is a mineral usually found with the above, and probably a product of their oxidation under the influence of air and water. It occurs as peach-coloured incrustations, giving a green streak, and it has the composition of a hydrated arseniate of cobalt, $Co_3As_2O_8.8H_2O$, and is found abundantly at Schneeberg, Saalfeld, and Riechelsdorf.

*Pyrolusite*, the black oxide of manganese, is often found to contain about 5 per cent. of cobalt, probably as peroxide.

*Skutterudite*, a sesquiarsenide of cobalt, $Co_2As_3$, has been found at Skutterud, in the parish of Modum, Norway, and analyzed by Scheerer and Wöhler.

*Mispickel*, the ordinary arsenical pyrites, sometimes contains upwards of 2 per cent. of cobalt.

*Cobalt pyrites*, $Co_2S_3$, also occurs in grey octohedra.

Nearly all the minerals of cobalt occur in crystalline slates or other metamorphic rocks, either in embedded crystals reticulated or finely dispersed; and the value of the ores varies extremely, and not only depends upon the percentage amount of cobalt, but on their freedom from other metals, excepting nickel, and the presence of the latter in sufficient quantity to make its separation remunerative.

Metallurgy.—This metal is never used in the arts in the metallic state, so that its metallurgy is completely confined to laboratory processes.

To obtain it, the oxide obtained by any of the processes given further on is first purified. It is dissolved in nitric acid for this purpose, and the cobalt separated by addition of nitrite of potassium solution to the neutralized solution of cobalt. Upon allowing to stand a yellow precipitate settles, which, after being washed, is dissolved in acid, and the cobalt precipitated as oxide by addition of an alkali, or as oxalate by oxalate of ammonium.

The purified oxide thus obtained is dried and mixed into a paste with oil, and inclosed in a charcoal lined plumbago crucible, which is covered, well luted, and then strongly heated in a forge fire. The oxide is thus reduced, and the metal fuses to a button at the bottom of the crucible. This button is a carbide of cobalt analogous to cast iron.

Chemically pure cobalt may be obtained from purpureo-cobaltic chloride, a compound ammonium salt, which is easily obtained pure. It is first ignited, and the cobalt chloride which then remains is heated to redness in a current of hydrogen.

Ignition of the oxalate in a well-covered crucible lined with lime, also affords a very ready means of obtaining this metal in a pure state. To obtain it fused, however, it must be heated to the highest possible temperature attainable by a forge fire.

*Properties.*—Pure cobalt is of a grey colour with a shade of red, and is by no means brilliant. Its texture varies according to the temperature employed in fusing it; sometimes it is composed of plates, sometimes of small fibres adhering to each other. It is very hard, and nearly as infusible as iron. Like iron it is attracted by the magnet at the ordinary temperature, but loses this property upon moderate heating. It can be magnetised permanently, and Pouillet states that this magnetism is not destroyed by a red heat. It cannot be fused in presence of charcoal without taking up some of the latter, and forming a compound analogous to cast iron.

By reducing the oxalate in a crucible lined with lime, Deville states that he obtained a metal which, when drawn into wire, was so remarkably tenacious as to be twice as strong as a similar iron wire.

At the ordinary temperature cobalt is permanent in the air, acquiring only a superficial tarnish, and it is also unacted on by water. But if heated to redness in the air it absorbs oxygen, and becomes converted into the oxide, the powder of which is at first blue, but becomes gradually deeper in colour and at last black, being then the peroxide, $Co_2O_3$, or the protosesquioxide, $Co_3O_4$, according to the temperature employed.

If very strongly heated the metal burns in the air with a reddish flame, and at a red heat it decomposes the vapour of water.

Hydrochloric and dilute sulphuric acids slowly dissolve it, forming the chloride and sulphate respectively. Nitric acid acts violently upon it, forming the nitrate.

The specific gravity of the metal is 7·834 (Turner), but has been very variously stated, and its specific heat is ·10696 (Regnault).

Alloys.—When alloyed with gold a dark yellow mass is obtained, which is very brittle when the cobalt is present in considerable proportion; but even with less than 2 per cent. of cobalt the resulting alloy is still brittle (Hatchett).

Silver does not alloy with cobalt, but when the two are fused together a layer of cobalt is obtained containing a little silver, and also one of silver rendered brittle by the presence of a small quantity of cobalt.

With zinc, lead, and bismuth, cobalt does not exhibit any tendency to alloy; but with iron a hard somewhat tough alloy results, and with tin a ductile metal is obtained, which has a violet tinge.

With platinum a fusible alloy is obtained, and with mercury a silver white amalgam.

Oxides.—There are two well-known basic oxides of cobalt, the protoxide, CoO, and the peroxide or sesquioxide, $Co_2O_3$. The protosesquioxide, $Co_3O_4$, is also a very definite body. It is here worthy of note that these oxides present a singular analogy to the oxides of iron, and this analogy is noticeable in many other of the compounds, properties, and reactions of this metal.

The protoxide is obtained by igniting the carbonate out of contact with the air in a well luted crucible, when it is obtained as a greenish grey powder, which dissolves readily in acids, forming the common cobaltous salts. All the definite salts of cobalt correspond to this oxide.

By addition of potash to a solution of any of these salts, a blue precipitate of a basic salt is thrown down, which, if protected from the air, changes immediately upon heating, or upon standing for some time, to a dingy red colour, becoming converted into the hydrated protoxide. But if exposed to the air the blue precipitate absorbs oxygen and becomes slowly converted into the peroxide, acquiring a greenish grey colour. The rose-coloured hydrated protoxide

also absorbs oxygen rapidly upon admission of air. The precipitate obstinately retains portions of alkali.

The sesquioxide of cobalt is obtained by passing chlorine through a solution in which the hydrated protoxide is suspended. Cobalt chloride is formed, and the peroxide remains as a black powder.

$$3CoH_2O_2 + Cl_2 = CoCl_2 + Co_2O_3 + 3H_2O.$$

It can also be obtained by adding solution of bleaching powder to a solution of a salt of cobalt.

There are three other oxides of cobalt intermediate between the protoxide and peroxide, viz., $Co_3O_4$, $Co_8O_7$, and $Co_8O_9$; but with the exception of the first one, which is a definite body obtained by ignition of cobaltous nitrate, they are unimportant.

*Commercial Oxide of Cobalt.*—For commercial purposes the oxide is obtained by one or other of the following processes:—

1. The speiss obtained by smelting the ore is first powdered, dissolved in nitric acid, or hydrochloric or diluted sulphuric acid. The solution is evaporated to a small volume to separate the bulk of the arsenic as arsenious acid, and then diluted and decanted from that substance. It has next to be treated (being still acid) with sulphuretted hydrogen, as long as any precipitate is thrown down. After filtration the excess of sulphuretted hydrogen is expelled by boiling, and carbonate of soda added while the liquid is still warm. The cobalt, nickel, and iron thus precipitated are digested (after being well washed) in a solution of oxalic acid added in excess. The ferric oxide is dissolved by the oxalic acid, while the oxalates of nickel and cobalt are left insoluble. These are then well washed, dissolved by digestion with warm aqueous ammonia, and the solution allowed to stand exposed to the air for some days. The greater part of the oxalate of cobalt is retained in solution as the ammonia evaporates, but the whole of the nickel is precipitated and carries with it a little of the cobalt, which, however, may be recovered by redissolving the precipitate in ammonia and repeating the exposure. The ammoniacal solution of oxalate of cobalt thus obtained is evaporated to dryness, and ignited in the air to obtain the oxide. This process, devised by LAUGIER, gives the oxide almost entirely pure.

2. BERTHIER, to shorten the process of passing sulphuretted hydrogen in the above process, recommends that carbonate of potash be added to the liquid in small successive quantities as long as the precipitate consists of iron. At first it is white from presence of arseniate of iron, and if there be not enough iron in solution to precipitate all the arsenic in this form, some solution of ferric chloride must be added to slight excess. By careful addition of the carbonate of potash the iron must be exactly removed.

The bismuth and copper are then removed by passing sulphuretted hydrogen through the acidified liquid, this process now requiring much less time; and the liquid, which contains the nickel and cobalt free from iron, is treated for their separation by any of the methods given.

3. Another process recommended by LIEBIG for the treatment of arsenical ores, depends upon the stability of the sulphate of cobalt. The finely divided and well roasted ore is added in small portions to three times its weight of bisulphate of potash, fused in an earthen crucible or iron pot. The pasty mass thus obtained is then strongly heated till fumes of sulphuric acid are no longer given off, and then it is poured out. When cool it is broken up and boiled with water, and the solution, after removal of the insoluble arseniate of iron and nickel oxide, is treated with sulphuretted hydrogen to separate copper, bismuth, and antimony. The precipitate is filtered off, and then carbonate of soda added to the filtrate to precipitate the cobalt. This precipitate, upon ignition in the air, gives oxide of cobalt; but it is liable to be contaminated with nickel, because the sulphate of nickel is not easily decomposed, and in presence of sulphate of potash still less easily. Care should be taken that there is an excess of iron present during the fusion, over that required to combine with all the arsenic, otherwise arseniate of cobalt will be formed, and cause loss of that metal by not dissolving when the mass is treated with water.

4. WÖHLER's method for obtaining cobalt from arsenical ores consists in fusing the powdered ore with six times its weight of a mixture of carbonate of potash or soda and sulphur in equal quantities. The temperature is not raised high enough to fuse the sulphide of cobalt produced. The arsenic and sulphur combine with the potassium, forming a soluble sulpharsenite which, on being treated subsequently with water, is washed out. After this washing the residue is again fused with the mixture and again exhausted with water, to further remove the arsenic, and the product thus obtained is dissolved in nitro-hydrochloric acid and treated with sulphuretted hydrogen, which removes copper, bismuth, and any remaining arsenic. Then it is filtered, and the filtered liquid treated for the separation of the cobalt from the accompanying iron, nickel, &c.

5. WACKENRODER gives a process for the preparation of cobalt from cobaltiferous manganese. The ore is dissolved in hydrochloric acid and sulphuretted hydrogen passed through the solution to precipitate copper and other metals; the liquid is then precipitated with an alkaline sulphide, and the precipitate digested with cold dilute hydrochloric acid, which dissolves the sulphides of iron, zinc, and manganese, but leaves the cobalt and nickel.

*Manufacture.* — On a large scale, the process adopted for the manufacture of cobalt oxide is usually a modification of that recommended by BERTHIER. The finely powdered and well roasted cobalt speiss is dissolved in strong hydrochloric acid, and the iron and arsenic precipitated together, as described in 2, by the gradual addition of milk of lime. The liquid is run off from the precipitate, treated with sulphuretted hydrogen, and again run off the precipitated sulphides, and the cobalt separated from it by the careful addition of solution of bleaching powder.

The oxide possesses the property of imparting an intense azure blue colour to glass and most vitrifiable bodies, and that to so great an extent that pure white glass is rendered sensibly blue by the addition of $\frac{1}{1000}$th part of the oxide, while $\frac{1}{2000}$th part communicates a perceptible azure tint.

It is in consequence of this property that the oxide is used in the potteries, and by enamellers and glassmakers, as a blue pigment for their glazes. For this purpose they mix it in proportions varying according to the tint required with a vitrifiable flux, and apply it to their wares mixed with some adhesive material. A formula for a blue, known in the potteries as china blue or royal smalts, is—

| | |
|---|---|
| Oxide of cobalt, | 1 part. |
| Pearl ash (free from iron), | 1 " |
| White felspar (ground), | 8 " |

When the painted articles are subjected to a heat strong enough, the flux melts and dissolves the oxide of cobalt, acquiring a blue colour.

A black colour, used by enamel painters, is obtained by calcining oxide of cobalt with borax, and mixing the black mass thus obtained with very finely powdered black oxide of manganese. When fused the mass is deep black. A mixture of manganese and cobalt oxides is sometimes used by glass makers to make a good black glass.

Principal Compounds.—Cobalt forms two classes of compounds corresponding to the two basic oxides, namely, cobaltous compounds, corresponding to CoO, and cobaltic, corresponding to $Co_2O_3$. Of these the cobaltous compounds are by far the most stable, and also most numerous, and to this class belong all the ordinary salts of cobalt.

*Cobaltous Salts* are red when containing water of hydration, but blue when anhydrous. Their solutions are of a light red colour when not too concentrated, and this colour they exhibit even when considerably diluted. They redden litmus paper. With the exception of the sulphate they are all decomposed at a moderate red heat.

The chloride is formed when cobalt is heated to burning in chlorine gas. The anhydrous salt thus obtained forms blue crystalline pearly scales, which exhibit but little tendency to dissolve in water and are greasy to the touch. They absorb water from the air, changing to red, and then dissolve readily. The chloride may also be obtained, crystallized in rose red hydrated crystals, by dissolving the metal or any oxide in hydrochloric acid and evaporating the solution. These crystals are not deliquescent, and when heated partially decompose, giving off hydrochloric acid and leaving a greenish blue mass, supposed by Berzelius to be an oxy-chloride; and this upon further heating yields a sublimate of the anhydrous chloride, and leaves an oxidized residue.

When very concentrated, the colour of cobalt chloride solution is blue; but when more dilute it is rose red, which upon heating or upon addition of concentrated hydrochloric acid, absolute alcohol, or any dehydrating agent, changes to blue. In dilute solutions the colour is a delicate rose pink, and it is perceptible even when the solution is very dilute.

*Sympathetic Inks.*—The dilute solution of the chloride forms a "sympathetic ink." Writing upon a piece of white paper with it the characters are practically invisible, but upon applying heat to the paper they appear of an intense blue colour, due to the production of the anhydrous salt, or an isomeric modification. Upon cooling the writing gradually fades, from the reproduction of the original hydrated salt. The heat applied must not be too great, or the salt will decompose and appear of a black colour, which will not disappear again.

If desired, the colour can be modified. Thus, addition of a small quantity of an iron or nickel salt will cause the writing to appear green instead of blue. Zinc sulphate gives a red colour, and copper sulphate a yellow. By using suitable solutions what are called magic landscapes are produced, which are invisible, but upon applying a gentle heat appear in their proper colours.

The bromide and iodide give analogous chromatic phenomena.

*Detection.*—Cobalt in solution is detected by the following reactions:—

Sulphuretted hydrogen in acid solutions produces no precipitate.

Sulphide of ammonium in alkaline or neutral solutions gives a black precipitate, the formation of which is much facilitated by the addition of chloride of ammonium. The precipitate is only dissolved with great difficulty by hydrochloric acid, but easily by warm nitro-hydrochloric.

Potash and soda precipitate blue basic salts, which upon boiling turn pale red or become discoloured by absorption of oxygen. The precipitate is insoluble in excess, but carbonate of ammonia gives a violet solution either with the basic salt or the red hydrate.

Ammonia produces a blue basic precipitate in excess, which readily dissolves, forming a red solution, which on exposure to the air becomes violet.

Ferrocyanide of potassium precipitates the green cobalt salt, which is insoluble in hydrochloric acid.

Cyanide of potassium gives a brownish white precipitate of cobaltous cyanide, easily soluble in excess. From this solution acids precipitate it again. When, however, the solution of cyanide is boiled after addition of a drop or two of hydrochloric acid (to liberate prussic acid), the cyanide of cobalt is converted into cobalticyanide of potassium. Addition of acid does not now produce a precipitate.

Tartaric (or citric) acid and then ammonia in excess gives a solution which on addition of ferricyanide of potassium turns deep yellowish red, or when very dilute, rose coloured.

Carbonate of baryta does not precipitate cobalt, but if bromine water in excess be first added, the whole of the cobalt is precipitated as peroxide after standing for some time.

Nitrite of potash added in excess to the solution rendered acid with acetic acid produces upon standing in a warm place a yellow crystalline precipitate; quickly in concentrated, only slowly in dilute solutions. This precipitate is soluble in water, but not

in solutions of potassium salts or in alcohol. This is a very characteristic reaction.

In the borax bead compounds of cobalt dissolve to a clear deep azure blue glass, either in the inner or outer blowpipe flame. This reaction is very delicate and characteristic. With too much cobalt the colour approaches black.

With carbonate of soda on charcoal before the blowpipe, cobalt is reduced to the metallic state. The solution of the globules in nitric acid is pink.

*Separation.*—The separation of cobalt from other metals presents considerable difficulty, particularly from nickel, with which it is not only closely allied, but also often associated.

Cobalt is found with iron, nickel, manganese, zinc, and other members of this group, in the precipitate produced in an alkaline solution, which has previously been treated in an acid condition with sulphuretted hydrogen, which will have removed any copper, tin, bismuth, arsenic, &c., that might have been present.

The precipitate produced by the sulphide of ammonium, which will be black if it contain cobalt (or nickel or iron), is dissolved in warm nitro-hydrochloric acid, and freed from sulphuric acid by addition of barium chloride. It is then neutralized and digested with carbonate of barium. The aluminic, ferric, and chromic oxides thus precipitated will carry down traces of nickel and cobalt if a sufficient quantity of ammonium chloride be not added. From the filtrate the cobalt is precipitated with nitrite of potassium. To perform this operation it is necessary first to evaporate the solution to a small bulk, and neutralize it with caustic potash. A solution of nitrite of potassium having been neutralized, or rendered slightly acid by addition of acetic acid, is then added to the cobalt solution and the whole allowed to stand for two days, during which a yellow precipitate separates. Any precipitate that appears at once is removed by dropping in acetic acid. The yellow compound, the potassio-nitrite of cobalt, is then filtered off, and to the filtrate more nitrite of potassium is added, to see if any further quantity of the cobalt precipitate is produced. FRESENIUS and H. ROSE state that this is by far the most exact method of separating cobalt.

Another method that may be adopted, when no manganese is present, is to take the solution filtered from the precipitate produced by barium carbonate, and to add to it an excess of bromine water (or else saturate it with chlorine). It must be very dilute, not more than a gramme of cobalt to 300 c.c. of water. Some freshly precipitated carbonate of barium is then added, and upon standing the whole of the cobalt is separated as peroxide, and may be estimated by solution in hydrochloric acid and proceeding as below, after separating the barium by addition of sulphuric acid. Traces of cobalt are usually left behind with the nickel.

*Estimation.*—When a salt of cobalt is precipitated with potash the precipitate invariably carries with it a portion of alkali, from which it cannot be freed either by boiling or washing. Hence it is impossible to use this precipitate for estimating cobalt. For even if it be reduced in a current of hydrogen to the metallic state, the alkali cannot even then be removed by boiling with water (FRESENIUS). When, also, the sulphide of cobalt is ignited with excess of sulphur in a current of hydrogen, the residue has a variable composition, according to the temperature employed.

But, on the other hand, the sulphate is a very stable salt, not easily decomposed by heat, and the metal itself is easily obtained by ignition of the oxide or chloride in a current of hydrogen. The residue left on ignition of the nitrate is also a very definite compound, corresponding to the formula $Co_3O_4$.

Hence the most satisfactory methods for the estimation of cobalt are the three following:—

1. Having separated the cobalt from other metals, and having it in solution as nitrate or chloride, evaporate the solution to dryness and ignite the residue in a stream of hydrogen to a very intense heat, and after cooling in the gas weigh the metal thus produced. In the case of the nitrate, when no other acid is present, the ignited residue may be weighed itself, and the cobalt calculated from the formula $Co_3O_4$.

2. Precipitate the cobalt as sulphide by means of sulphide of ammonium, taking care that a considerable proportion of ammonium chloride be present, otherwise the precipitation is imperfect; and also that the precipitate be washed with water containing sulphide of ammonium, and, at first, chloride as well. Dissolve the precipitate in nitro-hydrochloric acid, and evaporate to dryness in a porcelain dish, with addition of sulphuric acid. The sulphate thus obtained may be removed to a platina crucible and weighed after gentle ignition.

3. Finally, there remains the estimation of cobalt as nitrite of cobalt and potassium. The precipitate obtained, as described under the separation, is transferred to a weighed filter and washed with a 10 per cent. solution of acetate of potassium, the last portions of which are displaced by using alcohol of 80 per cent. strength. The precipitate is dried at 100° C. and weighed. It has the composition $K_3Co5NO_3.H_2O$, corresponding to 13·64 per cent. of metallic cobalt.

GIBBS and GENTH recommend that the precipitated nitrite be ignited, and the residue treated with sulphuric acid and again ignited. A mixture is thus obtained corresponding to the formula $2CoSO_4.3K_2SO_4$. This is more satisfactory to weigh than the potassio-nitrite itself.

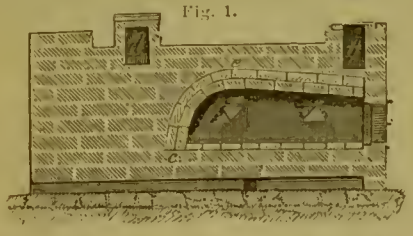
SMALT.—Smalt is a blue pigment very extensively used in the arts, consisting of potash-glass coloured with oxide of cobalt, and it is produced by fusing properly prepared cobalt ore with materials to form a suitable glass.

*Treatment of Ore.*—Arsenical cobalt ores are employed for the manufacture of smalt, and they first undergo a preliminary sorting by hand, by which the grossly impure portions are rejected. The selected ore is then powdered in a stamping mill, and the lighter siliceous and earthy parts removed

by washing. This treatment, however, does not separate the metallic impurities from the cobalt, so that it still contains the nickel, the antimony, &c., with which it existed in the matrix. But when bismuth is present it is first removed from the ore, before powdering, by liquation in iron tubes or retorts. (See BISMUTH.) Now these metallic impurities exercise a very hurtful influence upon the colour of the smalt, so that the next object in the treatment of the ore is to remove them.

*Roasting.*—This is effected by roasting the ores in a reverberatory furnace, with free access of air. The ores, the composition of which is, as before explained, chiefly arsenide and sulphide of cobalt, nickel, copper, and other metals, are oxidized by this treatment. The sulphur burns, forming sulphurous acid, which escapes, while the cobalt and other metals become partially converted into oxides; at the same time the arsenic also oxidizes to arseni-

Fig. 1.



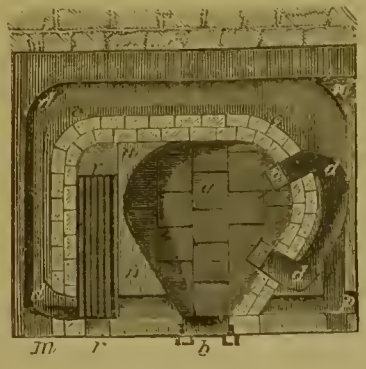


Fig. 2.

ous acid, which volatilizes and is carried away by the draught. The condensation of this arsenious acid must be effected in the process. Accordingly the manufacture is mostly pursued in winter, in order that the external cold may facilitate the operation, and the furnace employed is so constructed as to collect this volatile and poisonous product. Figures 1 and 2 represent this furnace.

The arch, *c c*, and the sole, *a*, of the roasting-hearth are formed of fire-stone. From 3 cwts. to 5 cwts. of "schlich" (pasty ore) are introduced by the roasting door, *b*, and serve for one operation; they are spread out in a uniform layer 5 or 6 inches in thickness, and this is then exposed to the flame of a fire on the grate, *r*. The flame passes over the fire-bridge, *n n*, and escapes with the volatile products through the flues, *o o*, into the common flues, *d d*, which encircle the fireplace. The orifices, *m m*, of these flues are only intended for the purpose of cleaning, and are usually closed; through the opening, *p*, on the contrary, the smoke enters a long smooth gallery (*poison gallery*), or a broad chamber sufficiently wide to impede the velocity of the draught and allow the arsenious acid time to collect and deposit.

Now, if we suppose the ore to contain no other metal than cobalt, it would evidently be most advantageous to carry the roasting to the utmost limit of oxidation, otherwise the unchanged sulphide and arsenide of the metal would be decomposed in the subsequent fusion, at the expense of a portion of the alkali, into sulphide of potassium and oxide of cobalt, or would subside as a cobalt speiss, causing loss of the metal in either case.

But by so dealing with the impure ores usually worked, nickel, copper, &c., would be converted into oxide, which by entering the smalt would spoil the colour, the nickel communicating a hyacinthine, the copper a red or green tint. The presence of some iron, however, would be of but slight importance, since it is deprived of colouring power by the addition of arsenic in the subsequent fusion, while upon nickel, zinc, and copper, the arsenic exerts no influence.

Hence, in practice, the roasting is not carried beyond a certain point, at which sufficient arsenic is left behind to combine with all the nickel; and, on the other hand, the oxygen absorbed is insufficient to completely oxidize all the metals. Consequently in the fusion those metals that have the most powerful affinity for oxygen, viz., cobalt and iron, will retain it persistently, while the others, copper, silver, and bismuth, will separate as a metallic regulus, and the nickel will combine with the arsenic, for which it has so great an affinity, and separate as a nickel speiss. Both of these products will be found under the layer of blue glass. If the roasting is continued for too short a period, a portion of the cobalt will remain unoxidized, and pass with the other metals into the speiss, when a loss of colouring matter will result: a *small* amount of cobalt in the speiss is, on the contrary, a good sign, indicating that the roasting has been sufficiently advanced, and yet that enough arsenic has been left to combine with the nickel, for which it has a stronger affinity than for cobalt. Arsenide of cobalt and oxide of nickel are mutually decomposed by fusion into oxide of cobalt and arsenide of nickel. Even with the utmost care some oxide of zinc will pertinaciously adhere to the cobalt, when it will communicate a greenish tinge to the glass.

As before mentioned, when the ores contain much bismuth, as is the case with those of the Erzgebirge, the greater part is extracted before they are employed in the smalt works, and the remainder is found below the speiss as the lowermost layer in the pots.

*Fusion.*—When the powdered ore, or "schlich," as it is called, has been roasted to the above-mentioned point, which is ascertained by observing when the deepest tinted glass is produced, in a test fusion on a small scale, it is then ready for making the blue glass.

Experience has shown the manufacturers that the presence of lime, alumina, and other earths, impairs the colour by diminishing its lustre and purity, and the fineness of the tint is still more damaged by soda. Hence, in selecting their fluxes, they are guided by these considerations, and fuse the prepared ore with addition only of potash and silica, both as pure as possible.

The silica is always used in the form of quartz, but is submitted to previous mechanical purification. For this purpose the quartz is heated to redness, and then disintegrated by quenching in water; it is then pulverized in a stamping mill, and the meal washed, suspended in water, and the fine powder allowed to subside. The lighter earthy and ferruginous particles remain longer in suspension, and can be poured off, and by repeating the process pure quartz-meal is at length obtained, which, when dried and heated to redness, is technically called *sand*.

In buying the carbonate of potash (pot ashes or pearl ash of commerce) great care is exercised in selecting such as shall not, as often is the case, contain sand, sulphate of magnesium, chloride of sodium, or sulphate of potash, and of course the usual tests of its alkalimetric strength and amount of moisture are made. Since it absorbs moisture from the air it is necessary to calcine it pretty strongly before using it, chiefly in order to facilitate its being well mixed with the other materials.

The mixture of the roasted ore with quartz and potassa is carefully conducted in wooden tanks, with the addition of white arsenic, which is essential on account of the iron in the ingredients; the arsenic is used in the form of powder, as it collects in the poison galleries, and with it a small portion of oxide of cobalt is recovered, which is mechanically carried over by the draught.

The proportions of the ingredients vary extremely, both with the richness of the ore and also with its quality, as regards siliceous and earthy matter, as well as with the depth of tint required. The depth of tint is also influenced, as before hinted, by other things than the amount of cobalt present. Thus lime and alumina, if present in the ore, will materially lessen the colour and degrade its purity. The difficulty of obtaining a uniform and constant blue will be evident from these facts, as it must entirely depend upon the nature of the ingredients; and these are subject to change in every consecutive roasting. As a constant quantity of potassa is always employed in the smalt works, proportionate to the sum of the other constituents of the mixture, viz., one-third the weight of the ore and sand together, the only question that remains to be settled is the relative proportion of ore and quartz.

This is decided by a repetition of the manufacturing process on a small scale. A small quantity of the roasted ore is fused with what is thought to be a sufficient quantity of the quartz meal and potash to produce the required tint, and the resulting glass observed carefully as to whether it is under or over coloured.

A series of definite tints, usually three, can thus be kept constantly on hand, and from these any desired tint can easily be obtained by mixing them in suitable proportions. A complete set of all the gradations of colour producible by the constituents is requisite for this purpose, and also a series of specimens of all the tints required in commerce. The desired colour is only obtained by accurately mixing the tints in the proper proportions, and hence they are always weighed in the dry state and never measured.

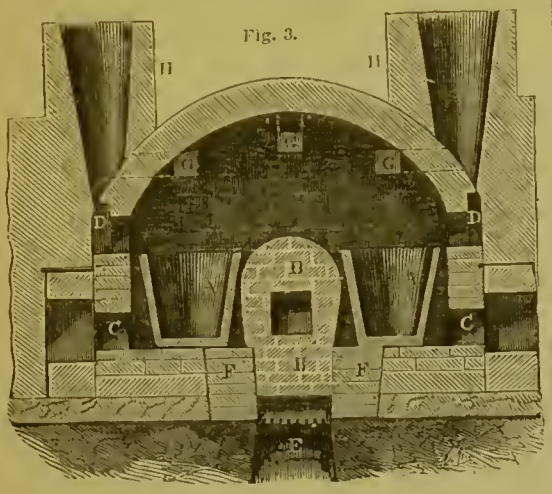
The operation of fusion is conducted in crucibles or pots, which are made of very refractory clay, containing no lime, and mixed with half its weight of dressed clay or cement. The mixture is well kneaded with water in a wooden trough, and the pots moulded, and then allowed to dry in the air. Afterwards they are very gradually heated to redness in a vaulted furnace, like a baker's oven, containing six crucibles at a time. If made too wet the pots crack on drying, and they split if they have not been thoroughly dried in the air. The best method of moulding them consists in beating the clay round a circular core, inclosed in a hollow cylinder, separated from the core by a distance equal to the thickness intended to be given to the crucible; the clay is heaped up gradually in small portions, and in the most uniform manner. The pots are a little conical, the larger circumference being at the upper part. They are 18 inches in diameter at top, 14 at bottom, and have a thickness of 2 inches. When they have been sufficiently exposed to the air, they are introduced into the furnace, and left there for from five to six days, during which the temperature is gradually raised to whiteness. Each pot is capable of holding about 84 lbs. of the mixture, and generally lasts seven or eight months.

The furnace in which the fusion is performed is similar to an ordinary glass oven; the separation of the speiss is the only essential difference in the process, and this gives rise to certain modifications in the construction of the furnaces, which are either circular, as at Schneeberg in Saxony, and Querbach in Silesia; or sometimes rectangular, as at Schwarzenfels in Hesse. They are adapted either for coal or wood. This will be more readily understood by reference to Fig. 3, which represents a German smalt furnace.

B is one of the openings for the insertion of the pots, which after this has been effected is walled up; the pots, A A, are pierced at the side with an orifice—speiss-hole—over against the *knee-hole*, C, for the withdrawal of the speiss. Through this opening the speiss and waste-glass are removed from the furnace, and the aperture is closed during the fusion. The working hole, D, is situated directly above, and serves for introducing and removing the ingredients and the glass. The flame is kindled on the grate, E, enters the furnace at F F, and passes out through the holes, G G G, which are in connection with the short chimney. Each pot, as before mentioned, holds about 84 lbs. of material, which is introduced by means of iron ladles furnished with long handles.

New pots are first filled with eschel, so as to coat the interior with a glaze. In the course of eight hours

Fig. 3.




the mixture enters into fusion, the workman occasionally stirring it up with a red-hot iron to break up the crust which forms on the surface. It is only when the molten mass is at a white heat that a chemical combination of the materials is effected; at this point the stirring must cease, and the heat be sustained, in order to aid the settling of the speiss.

Every time that the pots are recharged a depression of the temperature occurs, and it usually takes from an hour to an hour and a half to bring them back to whiteness. The furnace is said to work well if the pots glow, and the flame comes out briskly to the openings of the vault.

When the glass adheres to the workman's rod, and admits of being drawn into threads, or when it is homogeneous, it is ready for the next operation, which consists in ladling it out into a vessel full of water, kept cool by being repeatedly stirred. The vitrified mass falling in a molten state into water, becomes granular and easy to pulverize. If the potassa salt employed is pure, the scum, which is known as *glass-gall* or *sandiver*—impure sulphate of potassium—is not formed, but there is usually a portion to be skimmed off. When the cobalt contains nickel, an arsenide of this metal is produced, united with different metallic substances, which is deposited in the crucibles. A part remains even in suspension, so that in the Schneeberg works, when a pot is half emptied, they always expect to meet with globules of this alloy of cobalt, nickel, iron, arsenic, bismuth, and sometimes silver, which is known under the name of *speiss*. Every time that the workman draws off the blue glass, he allows this matter to deposit in his ladle, and before throwing the glass into water, he makes the speiss fall into an iron basin provided for its reception.

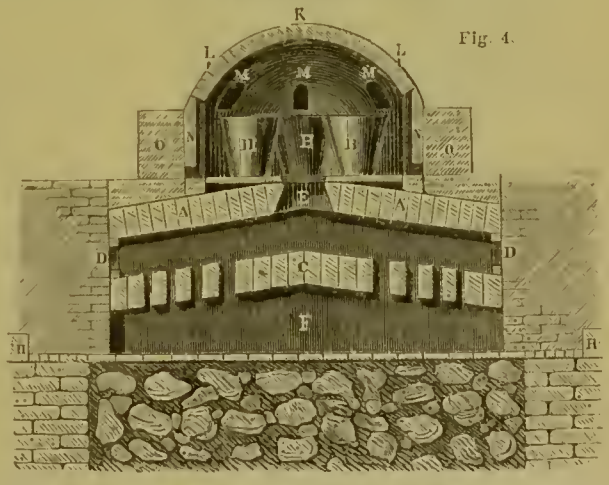
At Schwarzenfels each of the eight pots which the oven contains has in its lower part a small orifice, which is stopped up during the melting, but is opened when it is nearly completed. It is by this that the workman allows the speiss which is collected in the bottom of every pot to flow out. Then he draws off the blue glass. This, running out quite red hot into the basin of cold water, explodes, breaks into pieces, and becomes easier to pulverize. When a pot is empty, it is not refilled immediately; the glass is first drawn from all the other pots; because, while charging with new material, the furnace would cool, and the temperature being too much depressed, it would not be possible to empty the last pot completely.

When they are all empty, a recharging takes place, and the melting is continued in the manner described. The cold glass is withdrawn from the water, put to drain in a wooden trough, and carried to the store.

During the melting there forms what is called *verre de sole*, or waste glass; it proceeds from a part of the contents running over the pots, or spilling by the breaking of the vessel. This glass collects on the sole of the furnace, runs out by the opening for the flame, and mixes with the ashes; it is gathered up, crushed, washed, and serves for an addition to the charges in greater or less quantity.

A Swedish smalt furnace, such as is in use in Modum, is represented by Figs. 4 and 5. It resembles substantially the German furnace, consisting of a circular furnace chamber in which the crucibles stand, which is encompassed by the circular wall, O, and surmounted by a dome, K, which is strengthened by an iron ring, L. There are six working openings, M, in the dome, corresponding to the six crucibles, and also six openings, called knee-holes, in the circular wall.

Fig. 4.

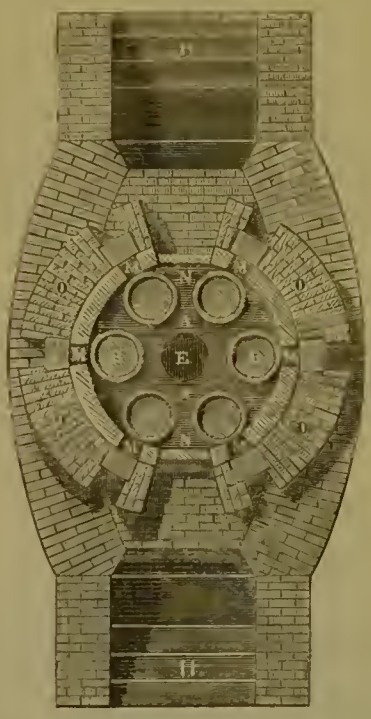



These serve for emptying the pots: there are besides two larger ones, N, through which the crucibles are introduced, and which are walled up during the working. The pots, B, stand on a floor supported on the crown of the furnace A; they are heated from below, the flames striking through the opening, E, from the brick grate, C, the stoke holes of which, D D, as well as the ashpit, F, is approached by the steps, H H.

The operation does not differ materially from the German process. A pot holds about 3 cwt., and the yield of glass is about 80 to 90 per cent., the loss consisting chiefly of carbonic acid and moisture, and the remainder being speiss.

*Grinding and Washing.*—The blue glass after being quenched in water is next broken up in a stamping mill, the stampers of which are shod with granite, and also strike upon granite; or it is crushed between rollers, and reduced to powder by two granite mill stones, working under water in a wooden trough. After grinding some hours an orifice in the wooden case, which envelopes the mill stones, is opened; when the ground material, mixed with water, escapes through a series of large troughs arranged to receive it. In the first it stays only a few minutes, during which the coarsest smalt deposits. This is known as strewing sand, or strewing blue, since it is sometimes used for sprinkling the floors; but only a part of it reaches the market for the purpose, the rest being ground again with fresh glass.

Fig. 5.



In the next depositing trough the liquid stays somewhat longer, and in the third about a quarter of an hour or more. The deposits in these troughs form the usual marketable smalt.

The product obtained in the fourth and fifth settling vessels forms an inferior quality known as *eschel*, having a lighter colour. The production of this, and of the still more finely divided and lighter portions, is to be attributed in some measure to the fact that the glass is attacked by the water and partially dissolved, notwithstanding the high proportion of silica in its composition. Carbonate and arseniate of potash are also dissolved. The liquid run off from the fifth trough is run into the sumpf or pool, and then allowed to settle entirely. The product obtained, sumpf-eschel, is a very slightly coloured substance, and is usually dried and resmelted in the pots.

The colours obtained in this manner are then each submitted to a further washing with fresh quantities of water in troughs. During this operation the workman agitates the mixture with a wooden oar, and then leaves it to settle; and afterwards, by means of a hair-sieve with close meshes, he frees the liquid from any floating impurities. The liquid thus prepared is again run into another trough, and allowed to settle.

The sediment or deposited colours have next to be dried. For this purpose they are removed from the troughs and put upon tablets, either in close chambers heated with a stove, or else in drying rooms exposed to the air. When properly dried the resulting mass has still to be crushed, as it is very compact. For this purpose it is passed between rollers and racks moved by water, or sometimes two planks sliding upon one another, or else an ordinary mill is employed.

The powdered colour is then sifted, usually through riddles which are inclosed in cases.

At Querbach, when the azure is drained it is withdrawn from the troughs, to which it strongly adheres, and is carried to the breaking benches, where it is pulverized with mallets and carried to the roller. After this it is taken to the braying machine, which is formed of two wooden cylinders turning horizontally. The azure is placed in a hopper, from which it falls upon the cylinders, which reduce it to a very fine powder. It is then dried in a stove chamber, in the centre of which is a furnace, the flame and smoke from which, after passing through a flue which runs round the drying bed, enters the chimney. The bed is terminated by a brick ledge 4 inches in height. The stove chamber is furnished with a number of shelves, upon which the smalt is first spread to dry, being frequently turned over upon them with a rake. The drying is completed upon the bed of the furnace. The temperature of the room is kept at 105° to 112° Fahr. When sufficiently dry it is again submitted to the action of the braying machine.

The anhydrous azure is finally submitted to a last manipulation. It is carried into a chamber containing a number of close cases bearing the number or symbol of each shade. In the middle is another tightly closed case, inside which a hair sieve, placed under a hopper, is suspended on an axis. The smalt is poured into the hopper and falls into the sieve, which the workman shakes by giving the shaft an alternate backward and forward movement.

The sifted smalt is put into packages, then closed up in small fir casks containing half a hundredweight, but before being packed it is damped with a little water to prevent loss of the dusty substance.

The yield of marketable blue producible from the blue glass is about 3 tons of azure, or dark blue, for every 5 tons of glass.

The following analyses of smalt are by LUDWIG. The Norwegian smalt was good and deep-coloured, and also the German high eschel, but the product given in the third column was an eschel only slightly tinted:—

| | Norwegian Smalt. | German Smalt. High Eschel. | German Smalt. Coarse Eschel. |
|---|---|---|---|
| Silica, | 70·86 | 66·20 | 72·11 |
| Oxide of cobalt, | 6·49 | 6·75 | 1·95 |
| Potash and soda, | 21·41 | 16·31 | 20 04 |
| Alumina | ·43 | 8·64 | 1·8 |
| Ferric oxide, | ·24 | 1·36 | 1·40 |

A good sample of smalt ought to contain not less than 12 per cent. of cobalt, and it should not effervesce on addition of hydrochloric acid, which would indicate adulteration with chalk. When washed with water it ought to settle completely in a short time; if the supernatant liquid is at all turbid, it should be examined for clay.

HENRY HUSSEY VIVIAN took out a patent in 1851 for improvements in obtaining nickel and cobalt. He found that these, in quantities of considerable value, were contained in copper ores, either the produce of foreign countries or of England, and that, in the treatment of such for copper, these metals have been wasted, a portion of them remaining in the refined copper and deteriorating its quality, another being thrown away in the slags, and a third being contained in a product called white or hard metal, commonly used in the manufacture of nails or sold at an inferior price. The object the patentee had in view was the separation of the above-named valuable metals, and obtaining them in a marketable form.

The invention consists in the separation of nickel and cobalt, or either of them, in the form of arsenides, from ores, slags, or regulus, and other combinations or alloys of copper, which is effected by means of the affinity of nickel and cobalt for arsenic, and of copper for sulphur. Arsenical pyrites is added to the cobaltiferous copper matter (white metal) and roasted. By this means an arsenical bottom is obtained, in which is collected all the cobalt and nickel.

The amount of cobalt ores raised in Great Britain is very small, almost the only mine that either does or has produced it being East Pool, in Cornwall. In 1871, 3 tons were raised, valued at £120, while in 1872, 1 ton only was produced, being worth £20; and in 1873, 8 cwts., value £12, was all the yield. None was obtained in 1874.

*History of Smalt Manufacture.*—According to the account of KLOTZSCH and LEHMANN, writing in 1650, the colour-mills were about a hundred years old, so that the invention would seem to fall about the year 1540. CHRISTOPHER SCHURER, a glass-maker at Platten, a place which belongs still to Bohemia, retired to Neudeck, where he established his business. Being once at Schneeberg, he collected some of the beautiful coloured pieces of "eobalt" which were found there, tried them in his furnace, and finding that they melted, he mixed some with glass metal, and obtained a fine blue glass. At first he prepared it only for the use of potters; but in course of time it was carried as an article of merchandize to Nuremberg, and thence to Holland; and as painting on glass was then much cultivated in Holland, the artists there knew better how to appreciate this invention. Some Dutchmen, therefore, repaired to Neudeck in order that they might learn the process used in preparing this new paint. By great promises they persuaded the inventor to remove to Magdeburg, where he also made glass from the cobalt of Schneeberg; but he again returned to his former residence, where he constructed a hand-mill to grind his glass, and afterwards erected one driven by water. At that period the colour was worth 7½ dollars (30*s.*) per cwt., and in Holland from 50 to 60 florins (about £4 to £5 of our money). Eight colour-mills of the same kind, for which roasted cobalt was procured in casks from Schneeberg, were soon constructed in Holland; and it appears that the Dutch must have been much better acquainted with the art of preparing, and particularly with that of grinding it, than the Saxons. In a little time more colour-mills were erected around Schneeberg, to the detriment of those at Platten. PAUL NORDHOFF, a Friedlander, a man of great ingenuity, who lived at the Zwitter-mill in Schneeberg, made a great many experiments in order to improve the colour, by which he was reduced to so much poverty that he was at length forced to abandon that place and to retire to Annaberg, where he established a colour manufactory by the aid of a merchant at Leipsic, of which he was made the director; and by these means rendered the Annaberg cobalt of utility.

This information is in some measure confirmed by MELZER, who says that the mines of Schneeberg, which were first discovered in the middle of the fifteenth century, had declined so much towards the middle of the sixteenth, that it was impossible to get any profit by them until the year 1550, when a greater advantage arose from the new method of using cobalt. About this period a contract was entered into with the Dutch, who agreed to take the roasted cobalt at a certain price. LEHMANN says, but without giving his grounds, that a manufactory for making blue glass was erected by SEBASTIAN PREUSLER between Platten and Eybenstoek, so early as 1571, while KOSLER, who died 1673, says that a century and a half before his time cobalt was sold as zaffre, but that the colour-mills in the country had been established only about sixty years (BECKMAN).

*Uses.*—Smalt has been employed in fresco painting and in the making of porcelain pottery, stained glass, encaustic tiles, &c. The paper manufacturer, who makes animal-sized papers for account-books, &c., also uses this substance to hide the otherwise yellow tint of his paper. BERZELIUS stated that the silicic acid contained in writing paper coloured with smalt blunted the points of steel pens. Paper tinted by smalt gives when calcined an ash having an azure blue colour, and often evolves when burnt the peculiar alliaceous odour due to the arsenious acid present in the smalt. There is usually some difficulty in keeping the smalt uniformly suspended in the pulp, so that one side of the paper thus coloured is generally darker than the other. Hence artificial ultramarine is often substituted in cheap papers, although it is not nearly so permanent.

A coloured glass like smalt is, of course, only attacked by agents which destroy glass, and as these

are so few in number, and so rarely occurring, smalt exceeds most pigments in chemical indestructibility and consequent permanency. It is applicable to all purposes for which a cheap durable blue is required. It is used by house-painters, by bleachers for finishing off cambrics, lawns, and linens, by the washerwoman for domestic purposes, and by starch-makers.

Good smalt may be used for painting on and colouring glass, but is not so appropriate for fine and delicate work as fluxes prepared with pure oxide of cobalt; while for less delicate purposes the simple mixture for making smalt will do as well as the prepared pigment. Indeed, large quantities of roasted ore, mixed with the proper proportion of quartz powder, are sent into the market for this purpose under the name of zaffre. The proportion of the ingredients in the zaffre must be arranged so as to give the tint required, and this is ascertained by a process of testing similar to that already described in the case of smalt. The names of *smalt*, *eschel* (from *ashe*, from the alkaline ash employed), and *zaffre* (corruption of sapphire) were originally applied to the same product, viz., smalt, but they have since been used to designate different substances.

A blue pigment has also been prepared by precipitating solution of cobalt (obtained directly from the ore) with a solution of silicate of soda. The silicate of cobalt thus prepared has been recommended as the compound best suited for painting upon glass and porcelain, and for the manufacture of blue glass.

Smalt is distinguished in the market by certain marks, denoting the depth and quality of the colour and fineness of the powder.

*Testing of Smalt.*—Smalt is very permanent under the action of reagents, and the quantitative testing of it is performed similarly to that of glass. Hydrochloric acid ought to act upon it only slowly, but upon boiling the smalt should become yellowish, while with caustic potash solution it should remain unchanged. It should also resist ignition, and fuse at a high temperature to a blue glass.

The following complete analysis of a good azure smalt by RIVOT will give some assistance in examining this colour:—

| | |
|---|---|
| Silica, | 56·4 |
| Alumina, | 3·5 |
| Ferric oxide | 4·1 |
| Cobalt oxide | 16·0 |
| Nickel oxide | None. |
| Lime, | 1·6 |
| Potash, | 13·2 |
| Lead oxide, | 4·7 |

*Thénard's Blue*, or *Cobalt Ultramarine*, is a beautiful blue pigment, one of the best and most permanent known. It consists essentially of alumina coloured by oxide or phosphate of cobalt. Its formation is used as a blow-pipe test for the presence of alumina; the supposed alumina being moistened with solution of nitrate of cobalt and ignited, gives a blue colour in the case of alumina, while zinc would give a green and magnesia a pink red colour.

The preparation of Thénard's blue is usually conducted by the following process:—A solution of cobalt nitrate is precipitated by addition of solution of phosphate of sodium, and the precipitate well washed by repeatedly agitating with water, allowing it to subside, and pouring off the supernatant liquid. A solution of alum is then precipitated by addition of a solution of carbonate of soda, and this precipitate is also well washed with large quantities of water, by decantation as before.

The pasty precipitates are then well mixed, in proportion varying a little, but usually about 5 parts of the alumina precipitate to 1 part of the cobalt phosphate. The mass must be well incorporated by long stirring, and then dried and ignited in a well covered crucible, from which great care must be taken to exclude the reducing gases of the furnace, otherwise the colour is much injured. To do this the more effectually it is usual to put into the crucible, along with the charge, a small quantity of red oxide of mercury, which, being decomposed by the heat into oxygen and mercury, fills the crucible with an oxidizing atmosphere, while the mercury volatilizes, doing no harm.

Another modification of the process of making this colour is to mix solutions of the nitrate of cobalt and the alum together, and precipitate this solution with carbonate of soda, and the precipitate thus obtained is treated as before. This is not so good as the previous method, because there will be some amount of alkali that cannot be removed by washing, and the colour produced is not so good as when phosphoric (or arsenic) acid is present. (LOUYET.)

The alum employed should be free from iron and zinc.

Another process consists in evaporating a mixed solution of cobalt sulphate and ammonia alum to dryness, and subjecting the residue to prolonged ignition to a high temperature in a wind furnace.

The colour of THÉNARD's blue very nearly approaches that of ultramarine, but it is more transparent, and by artificial light appears of a violet tinge, like most other of the cobalt colours. But THÉNARD'S blue is a much more permanent colour than ultramarine, and indeed than other blue pigments. It is unacted upon by either hydrochloric acid or potash solution, and of course withstands the most intense ignition; nor is it at all poisonous, except when prepared from arseniate of cobalt, or when arsenic has been added to improve the tint. THÉNARD'S blue is used by artists.

*Caruleum.*—Under this name a blue pigment, consisting of tin oxide coloured with cobalt, has been prepared by ROWNEY & Co., and has the advantage over THÉNARD'S blue of being less transparent, and in retaining its blue colour in gaslight. An analysis of the colour shows the following composition:—

| | |
|---|---|
| Binoxide of tin, | 49·66 per cent. |
| Oxide of cobalt, | 18·66 " |
| Silica and sulphate of lime, | 31·68 " |

It is attacked by hydrochloric acid and by nitric,

but is unacted on by caustic alkalies. It is used by artists both as an oil and a water colour.

*Rinmann's Green.*—According to WAGNER this pigment, which consists essentially of oxide of zinc coloured with oxide of cobalt, is prepared by precipitating a 10 per cent. solution of cobalt chloride with carbonate of soda, and mixing the washed precipitate with zinc-white to a reddish violet cream, which is then dried and ignited. There must be about nine times as much zinc as there is cobalt. Phosphate or arseniate of soda may be substituted for carbonate with beneficial result. Five parts of zinc-white to 1 of cobalt gives a deep dark green, but the above given proportions give a full grass-green colour. GENTELL recommends that alumina be mixed with the zinc oxide to the extent of 10 or 20 per cent.

The same qualities that recommend THÉNARD'S blue also apply to RINMANN'S green, viz., that it is unacted upon by caustic alkalies, hydrochloric acid, or by ignition. But it is attacked by ammonia. It is not poisonous when arsenic has not been used to prepare it, and in this respect is superior to most other green pigments.

*Cobalt Bronze* is a double salt of cobalt, phosphate of ammonia and cobalt, prepared at Pfannensteil, near Aue, in Saxony. It is a violet-coloured powder with a strongly metallic lustre, and resembles in general appearance the violet-coloured chloride of chromium.

*Silicate of Cobalt*, obtained by precipitating a solution of a cobalt salt with silicate of soda, is a blue powder that has been used for painting on porcelain.

*Cobalt Yellow* is the double nitrite of cobalt and potassium, for the preparation of which see "Separation of Cobalt." It has been used as a yellow colour in oil and water colour painting in consequence of its resisting the action of sulphuretted hydrogen and oxidizing agencies. It is also applicable, instead of cobalt oxide, as a blue pigment for the colouring of glass and for porcelain painting, and is to be recommended for this purpose because it is easily obtained in a pure state, and free from metallic oxides injurious to the colour.

**COCHINEAL.**—It is stated that as early as in the time of Moses the highly prized red colour used for dyeing the garment of the high priest was derived from an insect (*Jole*), which according to the accounts given appears to have been the same as that which later in Greece and Rome attained great importance, and continued to be the principal red colouring matter in the middle ages, especially amongst the Moors, long after the art of producing the Tyrian purple had died out. This insect is the *Coccigranum* of PLINIUS, or the *Coccus ilicis L.*, generally known by its Arabic name kermes, or alkermes. It lives upon the branches of the *Quercus coccifera L.*, a shrub of Southern Europe, Syria, and North Africa, and is only met with where this plant thrives.

Another species of *Coccina*, the *C. polonica*, which lives upon the roots of *scleranthus*, *herniaria*, and other plants in Northern Europe, was formerly collected and highly esteemed in Germany, Poland, and Russia, as a red dye; but on account of its sparse occurrence, was of much less importance than the former. Besides these there are other colour producing species, such as *C. uvae ursi* in Russia and *C. fabæ* in France, and last, but not least, the *C. lacca*, which furnishes the lac-dye and shellac.

Thus quite a number of species of this particular family of insects, the *Coccidæ* or *Gallinsecta* of the order of the *Hemiptera*, were known from the earliest ages, and made use of in the old world for the purpose of producing a red dye; but it was after the discovery of America that yet another, and by far the most important species, the cochineal, was introduced.

As a general characteristic of the whole tribe of the *Coccidæ* it may be mentioned that only the male insects are furnished with wings, whilst the females are wingless, very much larger, and generally of a largely extended spheroid shape; they are so stationary in their habit that, on first sight, their animal character may be often altogether overlooked. It is only the female insect which furnishes the dyeing material.

As a rule these insects affect only particular species of plants, and the females, generally in large numbers, fasten themselves on the more succulent parts, such as the leaves, young branches, and sometimes the roots.

Most of them produce and surround themselves with a peculiar secretion which exudes from their body, and which generally serves the purpose of a nest or shelter for the young brood. This secretion is in some cases of a viscid sugary nature; in others of a resinous character, as with the *C. lacca*, which in this way produces the shellac; but more commonly, as in the case of the cochineal and kermes, it appears in the form of a downy wool-like substance, composed of a special kind of wax similar to that which is produced by another species of this family, the *Coccus cerifera*, and known in commerce under the name of "Chinese wax." (See CANDLE.)

The cochineal insect is a native of Mexico, where it had been employed by the Aztecs and Tezcucans for an indefinite period for the production of a red colour, and it was even to some extent cultivated by them for this purpose. On the invasion of that country in 1518 the Spaniards soon recognized its great tinctorial value, and subsequently the demand from Europe for this new article caused a great increase in its production, which was brought about by means of regular plantations which were laid out in the southern provinces of Mexico, especially in Tlascala, Oaxaca, Yucatan, Guatemala, and Honduras, and it soon became one of the most valuable articles of export from this newly acquired country. Mexico maintained for a long time the monopoly in the production of cochineal, and the Spanish governments exercised great vigilance in preventing its introduction into other countries. In the middle of last century they had recourse to the strange expedient of decreeing the destruction of all the plantations in Yucatan, in order to raise the price of the cochineal.

It was not until in the second quarter of this

century that the cultivation of the cochineal insect was introduced into the south of Spain (Malaga and Valencia), Malta, Algiers, the Cape, Madeira, Java, and Teneriffe; but only in the latter island has it attained any importance, and indeed, at the present moment, more cochineal is exported from Teneriffe than from any other country.

Lopez de Gomara, in 1525, and Plumier, in 1692, gave the first description of the cochineal insect and the plant on which it lives; but nevertheless it was generally regarded as the seed of a plant, and this opinion continued prevalent, notwithstanding numerous publications on the subject by various authors, such as Lister, who in 1672 justly regarded it as a kind of kermes, Hartsoecker (1694), Leewenhoeck, who made a microscopical examination of it in 1703, De la Hire (1704), and Geoffroy (1714). At last all doubts were removed by Ruuschier* who, in the year 1729, obtained direct information from cultivators of cochineal in Oaxaca. About 1757 a Mr. Ellis obtained portions of the cactus plant, and observed that the specimens were full of the nests, in which the insect appeared in various states, from the most minute, when it traverses the plant, to the period when it fixes itself on the leaf. He also found by the assistance of the microscope the true male insect, in the parcels which had been sent to him from America; and in consequence of this discovery Dr. Garden caught in 1756 a male cochineal fly, which, he observes, is rarely to be met with. He supposes that there are from one hundred and fifty to two hundred females for each male.

The cochineal is only found upon certain species of cactus, such as *Cactus coccinellifer*, *C. opuntia*, *C. tuna*, and *C. Pereskia*.

Formerly a considerable proportion of the commercial cochineal was gathered from the wild growing plants; this was, however, of an inferior quality, and called *grana silvestra*. At the present time nearly all the cochineal which comes into the market is the produce of the regular cultivation of the insect, which is carried on in a systematic manner. This plantation cochineal is termed *grana fina*, *mestica*, or *mestique*.

The cochineal plantations are generally situated on slopes of valleys, or on hillsides which are sheltered against the cold winds. The season of rearing and gathering lasts about seven months, during which period the insects are collected three and sometimes four times.

The male insects resemble somewhat a middle-sized gnat, or still more the larger species of male aphides; they are of a red colour, and have two white wings. They fly about, and after having fructified the females, die. They live about four weeks, or half the time of the females. The females are very unlike the males, as they have no wings, and only move about when quite young, and still very small. They soon fix themselves with their proboscis upon the surface of the cactus leaves, and then assume a swollen spheroid shape, not unlike small dark red or purple berries, and begin to surround themselves with the peculiar white fluffy substance already referred to. In about two months they attain maturity, and then are gathered by being brushed from the plants with a feather, or a brush made of the stalk of a palm leaf, and killed at once, either by being immersed into boiling water or by being exposed to steam, or sometimes by being put on suitably heated plates. After having been carefully dried, they form the cochineal of commerce.

On the plantations special provision is made for securing a new crop by preserving at the end of the season branches of the cactus which are covered with female insects, and keeping them during the cold season under shelter. On the return of the warm season these females are put into small artificial nests, made of some downy or woolly looking material, and distributed over the plantation. As soon as the young insects are hatched they move about for a short time, and spread themselves over the cactus plants; however, they soon attach themselves on the surface of the leaves, as already mentioned, and in turn attain their maturity in about two months.

According to the condition in which the insects are gathered they lose from two-thirds to three-fourths of their weight on drying, and it requires from 40,000 to 60,000 insects to produce 1 lb. of dry cochineal. A plantation of about 2½ acres requires the attendance of three men, and yields from 500 to 600 lbs. of cochineal.

In the state in which the cochineal is found in commerce it bears hardly any resemblance to an insect, and judging from its appearance only, it is by no means surprising that the belief in its vegetable origin should have endured for so long a time.

The cochineal occurs in several distinct forms, which are now generally classed under three different denominations, namely, the grey or silver cochineal (*Jaspeada*), the black (*Negra*), and the shelly cochineal.

It is generally stated that this different appearance is simply due to the mode of killing and preparing the insects, and accordingly the silver cochineal is said to be obtained by drying the insects on hot plates or in ovens, whilst the black cochineal is produced by momentary immersion in boiling water and subsequent drying. The third variety, or shelly cochineal, generally of a dark reddish or brown colour, differs in other respects from the former kinds, as will be pointed out hereafter. This variety has been introduced in steadily increasing quantities during the last twenty years, but nothing reliable is known about its mode of production.

The cochineal appears in the form of somewhat irregular shrivelled up grains, wrinkled with deep contorted furrows, which in the case of the silver cochineal are more or less filled up with a white powdery substance, the remains of the peculiar downy secretion with which the insect surrounds itself; in the black cochineal this latter substance or white coating has been partly or nearly entirely removed by the process of immersing the insects into boiling water, and therefore the dried insect appears in its proper colour.

* Phil. Trans. vol. xxxv. p. 265.

The shelly cochineal, on the other hand, differs from the former very considerably. As its name indicates, the individual insects have the appearance of nearly empty shells, which show but few and much less pronounced wrinkles on the upper convex side, whilst the lower part is drawn in so as to form a concave depression.

In bringing cochineal in contact with warm water the grains generally float at first, but they soon swell up, and becoming quite soft and assuming gradually the spheroid berry-like shape of the live insect, sink under the surface. In this condition some of the characteristic insect features may be readily distinguished by the aid of a magnifying glass; remnants of the legs, the proboscis, and head, are often discernible, although these fragile parts of the insect have mostly been removed by the process of sifting and garbling to which the dry insects are submitted previous to their being sent into the market. To the unassisted eye, however, these swollen and softened grains present much greater resemblance to some kinds of berries, and this becomes still more striking when, on squashing or cutting them open, it is found that the thin skin incloses a soft dark-red pulp, in which generally a multitude of small grains are suspended, which might very easily be mistaken for seeds. In reality these grains are the eggs or young brood of the insect, and they form a very large portion of the bulk of the silver and ordinary black cochineal, whilst in the fine shelly cochineal they are either present in very much smaller numbers, or are wanting altogether. This seems to constitute the characteristic of the shelly cochineal, and it would follow from this that the shelly cochineal represents the insect in a different state of development. The better kinds of this variety do not show any sign of the white secretion, and consist of very large and regularly shaped insects, of a dark reddish-brown colour and smooth shiny surface. Other kinds consist of small, irregular, very thin, and light shells, of much inferior appearance, which, however, not unfrequently are found to be superior in yield of colouring matter to any other kind.

As the eggs do not contribute to the yield of colouring matter, it may be inferred that the heavy and solid-looking sorts of silver cochineal are by no means the most valuable; and this having been now pretty generally recognized, the preference is given to the shelly sorts. In Teneriffe, where of late years the cultivation of cochineal has made the greatest progress, about three-fourths of the cochineal produced is what is termed black shelly, and only one-fourth silver cochineal. In Honduras, on the other hand, four-fifths of the produce is silver cochineal.

Formerly the silver cochineal was considered to be superior, and not unfrequently the appearance of silver cochineal was imparted to other sorts by the application of some white powder, such as talc, carbonate of lead, &c. This and other sophistications of cochineal are now of very rare occurrence. Occasionally a parcel is met with from which part of the colouring matter has been extracted.

At the end of the season, when all the insects are removed from the plants, some are still small and imperfectly formed; these are, after drying, separated by sifting and sold as an inferior article under the name of "granilla."

It is generally supposed that the introduction of the aniline colours has very materially diminished the consumption of cochineal; but although this is no doubt true with regard to some special applications, the following table of importation to London during the last fourteen years shows, on the contrary, a slight increase.* From this table it will also be seen that Teneriffe produces now the largest quantity, whilst Honduras has fallen away considerably. London is by far the most important market for cochineal; Bordeaux, Havre, Marseilles, Amsterdam, and Rotterdam (the two latter places from Java), import now only small quantities:—

COCHINEAL IMPORTED INTO LONDON.

| Date. | Honduras. | Mexican. | Teneriffe. |
|---|---|---|---|
| | Lbs. | Lbs. | Lbs. |
| 1861 | 1,750,720 | 426,400 | 1,403,200 |
| 1862 | 1,188,000 | 129,600 | 1,155,680 |
| 1863 | 1,807,920 | 122,880 | 1,093,600 |
| 1864 | 1,274,080 | 372,480 | 899,520 |
| 1865 | 1,082,080 | 150,400 | 1,385,440 |
| 1866 | 966,240 | 197,760 | 2,019,680 |
| 1867 | 1,269,690 | 185 120 | 3,085,280 |
| 1868 | 529,920 | 271,520 | 3,106,080 |
| 1869 | 611,080 | 188,320 | 3,708,160 |
| 1870 | 614,880 | 300,480 | 3,903,520 |
| 1871 | 384,000 | 271,200 | 4,308,640 |
| 1872 | 362,240 | 199,360 | 3,082,080 |
| 1873 | 375,680 | 359,040 | 3,046,400 |
| 1874 | 417,440 | 394,720 | 3,041,120 |
| Totals..... | 12,636,180 | 3,569,280 | 35,238,400 |

As one of the most important dyeing materials, cochineal became the subject of chemical examination at a very early period, and in the course of time a considerable number of investigations were published by various chemists.

It was of course the colouring matter contained in the cochineal which chiefly attracted the attention of chemists; but although a good deal has been done towards making out the chemical history of this substance, much still remains to be cleared up in this respect.

As might be expected, the results of those researches which were carried out in the earlier part of this century are now of but little value; organic chemistry being then still in its infancy, the methods available for research were inadequate to deal with so complicated a subject. It may therefore suffice to give here merely a brief outline of the results obtained by the earlier investigators. Johann F. John published, 1813 ("Chemische Schriften"), the following analysis of cochineal, without however describing the method employed in separating the various constituents:—

* The use of kermes, on the other hand, has been discontinued now in Europe, and it seems to be no longer an article of commerce.

| | |
|---|---|
| Colouring principle (semi-solid, soluble in water and alcohol), | 50·00 |
| Gelatine, | 10·50 |
| Waxy fat, | 10·00 |
| Modified mucus, | 14·00 |
| Membrane, | 14·00 |
| Alkaline phosphates and chlorides, phosphates of lime, iron, and ammonia, | 1·50 |
| | 100·00 |

Pelletier and Caventou* communicated in 1818 a long memoir to the Institute de France, in which they described their results obtained in the chemical examination of cochineal. They first removed the fatty bodies by extracting the cochineal with boiling ether, in which the colouring matter was found to be but slightly soluble, and obtained by these means stearin, olein, and an aromatic acid, which, however, was not further examined. The exhausted residue was then treated with alcohol of 40° B., which dissolved the colouring matter, together with a small quantity of fatty and nitrogenous substances. On cooling this solution they obtained by spontaneous evaporation a granular red residue of a semi-crystalline appearance, and which they considered to be the colouring matter still contaminated with nitrogenous matter (*matière animalisée*) and some fatty substances, the greater part of which remained undissolved when treated with strong cold alcohol. By repeating this operation once or twice they considered that the substance was obtained almost in a state of purity. In order to remove the last traces of foreign matter it was dissolved in strong alcohol, and an equal volume of ether added, which precipitated the colouring matter and retained the fatty matter which was still adhering to it. The colouring matter thus obtained was named carmine (*carminium*). It is of a deep purple-red colour, very soluble in water, forming an intense purple liquid; in alcohol it is less readily soluble, and quite insoluble in ether and the fixed and volatile oils. The aqueous solution, when free from animal matter, is not precipitated by dilute acids, but its colour is changed to a yellowish red tint, which reverts to purple on neutralizing with an alkali.

Of the alkaline earths, lime only produces a precipitate: hydrate of alumina absorbs the whole of the colouring matter from an aqueous or alcoholic solution, but the presence of alum prevents this reaction. Neutral salts of lead merely change the colour of the solution to a violet; but the neutral acetate precipitates the colouring matter, forming a dark purple compound, from which the former can be recovered by decomposing the compound with sulphuretted hydrogen. These are the principal properties of the pure colouring matter of cochineal as obtained by Pelletier and Caventou. In a later communication (1832) Pelletier† gave the composition of the colouring matter as prepared by himself and Caventou, as follows:—

| | | | |
|---|---|---|---|
| Carbon, | 49·33 | Oxygen, | 40·15 |
| Hydrogen, | 6·66 | Nitrogen, | 3·56 |

* Annales de Chimie et Physique, ser. 2, tome viii. p. 250. Journ. de Pharm., ser. 2, tome iv. p. 193.

† Ann. de Chim. et d. Physique, ser. ii. tom. ii. p. 194.

T. Preisser, in an elaborate paper ("Rev. Scient." 16, 53) on the origin and nature of colouring matters, affirmed that he obtained by the action of sulphuretted hydrogen on the lead compound of the colouring matter of cochineal, a perfectly colourless well crystallized substance, which according to his statements was soluble in water and alcohol, but less so in ether, and assumed in contact with the atmosphere the purple red of the colouring matter of the cochineal. He also asserted that the aqueous solution of this substance gave, with acetate of lead, a white precipitate, which on exposure to the air assumed a purple tint. A. E. Arppe ("Liebig's Ann." vol. iv. p. 101) on repeating the experiments of Preisser, obtained a red solution, which on evaporation was converted into white crystals of oxalic acid, the formation of which was due to the action of nitric acid contained in the so called oxide of lead employed, which in fact was a basic nitrate. This explains to a certain extent the results of Preisser's experiments; but as regards his remarkable "chromogen," it may be assumed that in describing it he has rather drawn on his imagination. Arppe made some further attempts to separate the colouring matter in a pure state, but it would appear from the description of his mode of proceeding that he was unsuccessful.

Subsequently this subject was taken up by Warren de la Rue,‡ and submitted to a careful examination, which led to the separation of the colouring matter in a pure state, and the discovery of the nitro-coccusic acid.

After repeating the experiments of the former investigators on a considerable scale, in order to obtain the colouring matter in quantity, W. de la Rue devised the following method for separating this substance in a pure state. The aqueous decoction of cochineal is precipitated with acetate of lead, the bulky dark purple-coloured compound is washed by decantation with boiling distilled water, and then decomposed by sulphuretted hydrogen. The deep red liquid so obtained is freed from sulphuretted hydrogen by boiling, and then precipitated a second time with acetate of lead previously mixed with some acetic acid; the precipitate, after having been thoroughly washed as before, is decomposed with sulphuretted hydrogen. The liquid after filtration is evaporated on a water bath to dryness, and the dark residue dissolved in absolute alcohol. In order now to remove the small quantity of phosphoric acid which is still contained in this product, the alcoholic solution is digested with about the fourth part of the lead precipitate, which has been reserved for this purpose from the second precipitation, and after drying has been reduced to a fine powder. The alcoholic solution is then filtered, and after a part of the alcohol having been distilled off, is mixed with an equal volume of ether, which throws down a red flocculent matter containing some nitrogenous impurities still retained in the liquid. After filtration and distilling off the alcohol and ether, the substance remains behind in a pure state.

‡ Mem. and Proceed. of the Chem. Soc. Part xxii. 1847.

When thus prepared the colouring matter of cochineal forms a purple brown friable mass, transparent when viewed under the microscope, easily pulverized to a fine red powder, soluble to any extent in water and alcohol, but only slightly so in ether, which, however, does not throw it down from its alcoholic solution when it is free from nitrogenous matter.

This substance, possessing well marked properties, was named by W. de la Rue *carminic acid*.

Pure carminic acid is soluble without (?) decomposition in concentrated hydrochloric and sulphuric acids. Its aqueous solution is decomposed by chlorine, iodine, and bromine, which change its colour to yellow, and the latter, on warming or by standing, gives a yellow precipitate soluble in alcohol. Nitric acid even in a highly diluted state decomposes it, giving rise to the formation of oxalic and nitrococcusic acid. It bears a temperature of 136° C. without decomposition; on gradually increasing the temperature a quantity of an acid liquor is produced, and at red heat it intumesces and gives off a small quantity of red fumes, which condense; it gives no trace of oily matter.

The fixed alkalies and ammonia change the scarlet red colour of its aqueous solution to a deep purple; on mixing alcoholic solutions, however, purple precipitates are produced, which are the compounds of carminic acid with the alkaline base.

The alkaline earths produce with the aqueous solution likewise purple precipitates; sulphate of alumina gives no precipitate, but on addition of a drop of ammonia the carminic acid is precipitated in combination with alumina, forming a beautiful crimson lake; acetates of lead, copper, zinc, and silver, give purple precipitates. The latter is, however, immediately decomposed, and metallic silver is deposited; the nitrates of lead, mercury, and silver give reddish precipitates; protochloride and bichloride of tin do not form any precipitate, but change the colour to a deep crimson.

It is a matter of great difficulty to obtain even the insoluble metallic compounds of carminic acid in a pure state and of constant composition, for it appears that they carry down some of the precipitants. Only the copper salt could be obtained in a sufficiently pure state to serve for analysis and the determination of the atomic weight of carminic acid.

As the mean of several analyses W. de la Rue obtained the following percentages:—

| | | Theory. | Experiment. |
|---|---|---|---|
| $C_{14}$ | 168 | 54·19 | 54·13 |
| $H_{14}$ | 14 | 4·52 | 4·62 |
| $O_8$ | 128 | 41·29 | 41·25 |
| | 310 | 100·00 | 100·00 |

which led him to the adoption of the formula $C_{14}H_{14}O_8$, with which the results obtained by the analysis of carminate of copper also agreed:—

| | | Theory. | Experiment. |
|---|---|---|---|
| $C_{14}$ | 168 | 48·05 | 47·62 |
| $H_{14}$ | 14 | 4·01 | 4·12 |
| $O_8$ | 128 | 36·61 | 36·74 |
| Cu() | 39·6 | 11·33 | 11·52 |
| | 349·6 | | 100·00 |

Schützenberger (1858, "Ann. Chim. Phys." (3), vol. liv. p. 52), who subsequently investigated carminic acid, noticed a considerable difference in the composition of carminic acid of different preparations, and arrived at the conclusion that the carminic acid, as obtained by W. de la Rue, although otherwise pure, was a mixture of several substances. He found that by adding to a concentrated solution of carminic acid in absolute alcohol five or six times its volume of ether a red substance was precipitated, and on evaporating then the pale coloured alcohol-etheric solution a crystalline mass, composed of red needles and dark red granular crystals, was obtained. With boiling ether, which dissolves the latter, these two substances could be separated, and on being finally submitted to analysis the needle-shaped crystals gave numbers which agreed with $C_9H_8O_6$ (oxycarminic acid), whilst the granular crystals appeared to be $C_9H_8O_5$ (carminic acid.) Schützenberger considers it probable that several other coloured substances are contained in the carminic acid as originally prepared by W. de la Rue.

Later C. Schaller ("Bull. Soc. Chim." (2) vol. ii. p. 414: 1864), prepared carminic acid by precipitating the aqueous extract of cochineal with neutral acetate of lead, acidulated with acetic acid, and decomposing the thoroughly washed precipitate with sulphuric acid; the filtrate was then precipitated a second time, and the precipitate again decomposed with sulphuric acid, but carefully avoiding an excess of sulphuric acid in order to retain the phosphoric acid in the precipitate; the filtrate was now precipitated a third time, and the well-washed precipitate decomposed with sulphuretted hydrogen. After filtration the red liquid was evaporated to dryness, and the residue dissolved in absolute alcohol, when on spontaneous evaporation the carminic acid separated in crystalline nodules, mixed with yellow six-sided tabular crystals of another substance. Cold water dissolved the carminic acid, and left the latter undissolved; by evaporating the aqueous solutions and crystallizing the residue once more from absolute alcohol, the carminic acid was obtained in a pure state. The carminic acid prepared according to this method, on being analyzed, gave numbers which lead to the formula $C_9H_{10}O_6$, which differs from Schützenberger's formula only by $H_2O$. Schaller considers the carminic acid as a bibasic acid forming acid $\left.\begin{matrix}C_9H_8O_5\\ MH\end{matrix}\right\}O$, and neutral, $\left.\begin{matrix}C_9H_8O_5\\ M_2\end{matrix}\right\}O$, salts. The neutral sodium salt is obtained as a precipitate by mixing solutions of carminic acid and caustic soda in absolute alcohol. From an aqueous solution this salt crystallizes in nodular masses. On submitting a solution of carminic acid to the action of nascent hydrogen a colourless liquid is obtained, which resumes its red colour on exposure.

Although the results obtained by De la Rue, Schützenberger, and Schaller, agree well with regard to the general properties of carminic acid, it will be seen that they differ very materially with regard to the composition. The different formulæ derived from the results of analyses require:—

| Schaller. | De la Rue. | Schützenberger. |
|---|---|---|
| $C_9H_{10}O_6$ .... | $C_{14}H_{14}O_8$ .... | $C_9H_8O_5$ |
| C 50·5 p. cent. .... | 51·1 p. cent. .... | 55·1 p. cent. |
| H 4·7 p. cent. .... | 4·6 p. cent. .... | 4·1 p. cent. |

These discrepancies are too considerable to be ascribed to mere accident, and, indeed, can only be accounted for by assuming that the colouring matter of cochineal is a mixture of several very similar substances. Further examination being therefore required to clear up this subject—

Hlasiwetz and Grabowski ("Liebig's Ann." 141, p. 329: 1867), took up this investigation, and succeeded in establishing the important fact that carminic acid is a glucoside, for on treating it with boiling dilute acids it was found that it splits up into a peculiar kind of sugar and a new substance, which they named *carmin-red*. By effecting this decomposition it was clearly proved that none of the formulæ hitherto proposed expressed the true composition of carminic acid.

Hlasiwetz and Grabowski proceeded in the following way:—The precipitate of carminate of lead produced by acetate of lead in a filtered decoction of cochineal, after having been well washed, was decomposed with dilute sulphuric acid. To the dark red filtrate, after having been freed from lead by sulphuretted hydrogen, was added a small quantity (10 c.c. acid to the liquid obtained from 1 lb. of cochineal) of sulphuric acid, and then boiled for several hours. From the apparently unchanged liquid the sulphuric acid was now removed. By the careful addition of carbonate of barium, and after filtration, the liquid was precipitated with acetate of lead. This lead precipitate contained the carmin-red, whilst in the liquid the sugar remained dissolved. The liquid having been freed from lead by sulphuretted hydrogen was evaporated at a low temperature until a syrupy residue was left; this was found to be a mixture of the new sugar with a barium compound of the same, which could be separated by means of alcohol.

The analyses of these substances gave numbers agreeing with the formulæ, $C_6H_{10}O_5$ (dried at 50°), $C_6H_8O_4$ (dried at 100°), and $C_6H_9BaO_5$ (dried at 100°).

In order to separate the carmin-red from its lead compound it was found advantageous to effect the decomposition with dilute hydrochloric acid. The resulting red solution having been filtered off from the chloride of lead is freed from some dissolved lead by sulphuretted hydrogen, and then evaporated at a gentle heat.

Carmin-red so prepared forms a dark purple mass, which shows a green colour in reflected light; its powder is dark vermilion red, readily soluble in water and alcohol with red colour, but insoluble in ether. On being burnt it leaves a trace of ash, which contains lime, phosphoric acid, and a trace of iron. Its analysis led to the formula $C_{11}H_{12}O_7$.

The properties of this substance very much resemble those of carminic acid; it forms dark purple saline compounds with the alkalies, which are insoluble in alcohol, but soluble in water, with a violet colour, and these solutions give, with the chlorides of calcium, barium, strontium, zinc, &c., dark violet precipitates.

Several of these compounds (dried at 130°) were analyzed, and gave numbers agreeing with the following formulæ:—

$$C_{11}H_{10}K_2O_7, \quad C_{11}H_{10}BaO_7,^{*} \quad C_{11}H_{10}CaO_7.^{\dagger}$$

According to these results carminic acid must be considered a glucoside, and on assuming that its decomposition by acids takes place, as is invariably the case with this class of substances, under assimilation of water, this reaction may be represented by the following equation:—

$$\underset{\text{Carminic acid.}}{C_{17}H_{18}O_{10}} + 2H_2O = \underset{\text{Carmin-red.}}{C_{11}H_{12}O_7} + \underset{\text{Sugar}}{C_6H_{10}O_5}.$$

The formula $C_{17}H_{18}O_{10}$ for carminic acid requires C 56·1 and H 4·4, which are nearest approached by the results of Schützenberger's analysis.

Further investigation is, however, required to find a proper interpretation for the crystallized carminic acids observed by Schützenberger and Schaller.

*Nitro-coccusic acid.*—As already mentioned, carminic acid is readily acted on even by dilute nitric acid under violent evolution of nitrous fumes. The red colour of the carminic acid is instantly destroyed, and changed into orange. On bringing the action of the nitric acid to a termination by the application of heat, and keeping the mixture for some time at the boiling point, the resulting yellow liquid, after sufficient concentration, solidifies on cooling to a crystalline mass which, besides a large quantity of oxalic acid, contains the nitro-coccusic acid. In order to separate the latter, this crystalline mass is dissolved in a large quantity of boiling water, and a solution of nitrate of lead is added as long as a precipitate of oxalate of lead is formed. After filtering, the yellow liquid is evaporated, when some more oxalate of lead separates, which is removed, and after further concentration the nitro-coccusic acid crystallizes on cooling. By repeated recrystallization from water it is obtained in a pure state. Liebermann and Van Dorp have found it advantageous to use carmine instead of carminic acid, as De la Rue has done, for the preparation of this acid: and for the purpose of separating the oxalic acid they found it more convenient to dissolve the mixed acids in hot water, and then add some nitric acid, which causes the nitro-coccusic acid to separate on cooling, as it is but very little soluble in water containing nitric acid.

The nitro-coccusic acid is of a pale straw colour, or, if quite pure, colourless, crystallizing in rhombic plates, but exhibiting very different aspects according to the circumstances under which it is crystallized. It resembles somewhat picric acid (Trinitrophenol), and like this substance stains skin, wool, &c., yellow. It is soluble in cold, but more so in hot water, soluble in alcohol, and very soluble in ether; all these solutions being of a deep yellow. On being heated the acid deflagrates violently

* Ba = 137. † Ca = 40

Nitro-coccusic acid forms well crystallized salts of a deep yellow or orange colour; they are all readily soluble in water, and most of them in alcohol; and when heated to near 200° decompose with more or less violence. De la Rue by numerous analyses of the acid, and several of its salts, conclusively proved its formula to be $C_8H_5(NO_2)_3O_3$, and its salts $C_8H_3(NO_2)_3M_2O_3$. On boiling the aqueous solution of the acid with an excess of oxide of silver carbonic acid is evolved and a new acid is formed, which, however, has not been fully analyzed (probably Trinitrocresol). It will be noticed that the composition of nitro-coccusic acid bears no direct relationship to that of carminic acid, and taking into consideration that, according to Liebermann and Van Dorp, only about 8 per cent. is obtained, whilst a very large quantity of oxalic acid is produced simultaneously, it becomes evident that nitro-coccusic acid is not a direct derivation, but the product of a more complex reaction.

Nitro-coccusic acid has the same formula as trinitroanisic acid, but De la Rue has already shown that it is not identical with this acid.

Liebermann and Van Dorp, who have recently re-examined this acid, succeeded in clearing up its chemical relation by effecting its decomposition by heating it with water in sealed tubes to a temperature of 180°. Under these circumstances it splits up into carbonic acid and trinitrocresol, the latter being identical with that which Duclos obtained from coal-tar cresol.

Accordingly, nitro-coccusic acid is in reality one of the several isomeric forms of trinitro-cresotinic acid, and the above reaction corresponds with the decomposition of cresotinic acid into carbonic acid and cresol when heated, as observed by Kolbe and Lautemann—

$$C_8H_8O_3 = CO_2 + C_7H_8O.$$
$$C_8H_5(NO_2)_3O_3 = CO_2 + C_7H_5(NO_2)_3O.$$

*Coccinine* ($C_{14}H_{12}O_5$.). — Hlasiwetz and Grabowski obtained this remarkable derivative by submitting carmin-red or carminic acid to the action of fused potash. It is prepared by adding 1 part of these substances to 3 parts of caustic potash (when carminic acid is employed, 4 to 5 parts) dissolved in a little water, and heating the mixture carefully in a silver basin until the black colour has changed into a brown, and dissolves with a golden brown colour in water. The fused mass is then dissolved in water super-saturated with sulphuric acid, and after filtration the acid liquid is repeatedly shaken up with ether. The etheric solution leaves on distillation a crystalline residue, which after recrystallization from alcohol furnishes the coccinine in a pure state. When carminic acid, instead of carmin-red, has been employed, oxalic and succinic acids are obtained along with the coccinine, and are removed by washing with water. The yield of coccinine at the best is but small, and depends very much on the care with which the operation is carried out.

Coccinine crystallizes in yellow rectangular plates, which are insoluble in water, readily soluble in alcohol, but less so in ether. In dilute alkalies it dissolves with great facility, forming yellow solutions which, on contact with the air, turn at first green, and then this colour gradually passes through violet into a beautiful purple red. The alcohol solution when brought in contact with sodium amalgam turns likewise green, but on subsequent exposure to the air assumes a deep indigo colour, and deposits an amorphous substance of the same colour. Coccinine appears to form definite compounds with bases of a pale yellow colour, but they are so changeable that they could not be obtained in a pure state.

*Ruficoccine* ($C_{16}H_{10}O_6$.).—According to Liebermann and Van Dorp carmin-red and carmine dissolve in concentrated sulphuric acid without change, but on heating the solution to 125° the colour changes into a violet; and if after the temperature having been kept for several hours at 130° to 140° the liquid is poured into water a dark precipitate is produced, which is composed of ruficoccine and another new substance. After thorough washing with water and drying it is exhausted with boiling alcohol, which on evaporation leaves the ruficoccine. After repeated washing with water and recrystallization from alcohol this substance is obtained in the form of a brick-red powder. It is but very little soluble in water; but on heating it in a sealed tube with water to 200°, on cooling a voluminous mass of orange-coloured needles is obtained.

Ruficoccine is but sparingly soluble in ether, but dissolves more freely in alcohol. These solutions show a fine greenish yellow fluorescence. It is readily soluble in alkalies, forming at first brown or brown-red solutions, which, on the addition of an excess of alkali, assume the colour of the rosaniline salts. The calcium compound is a dark violet precipitate; when dry a black powder, having the composition $C_{16}H_8CaO_6$. In concentrated sulphuric acid ruficoccine dissolves with a violet red colour. When heated it gives off red fumes and yields a small quantity of a red sublimate. By heating ruficoccine with zinc dust a solid hydrocarbon is produced, which sublimes in white plates, melting between 183° and 188°. By oxidation this hydrocarbon, which appears to be $C_{16}H_{12}$, yields a quinone resembling anthraquinone, but melting at 250°.

The quantity of ruficoccine produced by the action of sulphuric acid on carmine amounts to about 10 per cent., whilst of the insoluble bye-products mentioned above as much as 30 per cent. are obtained. This latter substance is a black powder which dissolves in the alkalies, and appears to have the formula $C_{32}H_{20}O_{13}$. When heated it chars and does not yield any hydrocarbon on being heated with zinc dust. With nitric acid it furnishes, however, nitrococcic acid and oxalic acid. On being heated with a solution of baryta for five or six hours a solution is obtained which gives, with hydrochloric acid, a brown precipitate soluble in alcohol, ether, and benzol, and with violet colour in the alkalies. This substance heated by itself gives off red fumes, and with zinc dust furnishes a hydrocarbon which appears to be identical with the one obtained from ruficoccine.

*Ruficarmine*, $C_{16}H_{12}O_6$.—On heating an aqueous solution of carmin-red in a sealed tube to 200°, its dark red colour changes into yellow, whilst a dark resinous body is deposited. This substance differs from carmin-red by its insolubility in water, and from ruficoccine by its great solubility in alcohol and ether: in the alkalies it dissolves, like these substances, with violet colour. As obtained by the precipitation of the alcoholic solution, by careful addition of water and a little hydrochloric acid, it forms a beautiful red powder.

On evaporating the aqueous extract of cochineal, from which the colouring matter has been removed by precipitation with acetate of lead, there remains a dark-coloured, syrupy liquid of a very complex character. If the concentrated liquid is allowed to stand for a while a white chalky matter subsides, which was originally recognized by W. DE LA RUE, and identified with *tyrosine*.

Besides this, several other crystalline substances, generally met with in animal extracts, have been noticed, as for instance *guanine* and *inosite*, which both appear to be present in not inconsiderable quantities; and on working with larger quantities of cochineal, for the purpose of preparing carmine or other colours, these otherwise rare substances may be obtained with advantage from this source. (HUGO MÜLLER).

*Cochineal Wax, or Coccocerine.*—The peculiar downy, wool-like secretion with which the female cochineal insect surrounds itself, and which is found to some extent still adhering to the silver cochineal and causing its white chalky appearance, is a kind of wax, which, however, differs from all known substances of this kind by its sparse solubility in the ordinary solvents and its high melting point. This cochineal wax, or *coccocerine*, is best obtained by treating silver cochineal, or, still better, the siftings of this article, with boiling benzol or its higher homologues, in which it is readily soluble. On cooling it separates almost entirely from this solution, and by repeated crystallization from the solvent it may be obtained in minute colourless crystals melting at 105° C. In alcohol and ether this substance is but very little soluble, and it is probably on this account that it was considered formerly to be of a mineral origin. In chloroform and disulphide of carbon, especially when hot, it is readily soluble. A solution of alcoholic potash saponifies the coccocerine and separates coccocerylic alcohol, whilst coccocerate of potash remains in solution. Concentrated sulphuric acid effects a similar decomposition. (HUGO MÜLLER.)

*Spectroscopic Character of the Colouring Matter of Cochineal.*—It is a matter of considerable interest that an aqueous extract of cochineal, although not showing by itself any characteristic features when examined by the spectroscope, on addition of ammonia, which turns the scarlet tint of the solution into a violet, exhibits two dark absorption bands between the FRAUENHOFER lines D and E, like those of blood, one situated at 8° the other at 9°—10° of a spectroscope having a scale of 20°, in which the sodium line falls at 7·7. (CAMPANI, *Gazzetta Chimica Italiana*, i. 471).

*Valuation of Cochineal.*—It is obviously impossible to judge positively of the quality of cochineal by its physical characters only, or in other words to estimate the amount of colouring matter contained in it by mere ocular inspection, yet this is still the common practice in commerce.

Various methods have been proposed for estimating the value by chemical means, which however, although simple enough, do not seem to furnish reliable results. The quantitative determination of the colouring matter by direct methods not being attainable, recourse must be had to comparative experiments. Accordingly the results of all these processes are obtained by comparing with standard specimens of cochineal the amount of particular reagents required, either to destroy or to remove the colour from the decoction of the weighed sample to be examined. For this purpose ROBIQUET proposed a solution of bleaching powder; PENNY a mixed solution of ferricyanide of potassium with caustic potash. In both these methods the colour is destroyed; on the other hand, ANTHON precipitates the colouring matter with alumina, and in a similar manner BLOCH makes use of a standard solution of acetate of lead.

From what has been said about the complex composition of cochineal, and also of the colouring matter itself, which appears to be a mixture of several substances, it is obviously very unlikely that these chemical methods can give any reliable results; for, quite apart from the fact that there are along with the colouring matter substances contained in the cochineal, which are in a like manner affected by the reagents employed, it is more than probable that also the tinctorial qualities of the several colouring matters contained in cochineal vary considerably. Consequently a method, to be of any practical value, would be required to take also cognizance of the relative quantities of the substances which constitute the colouring matter, with our present knowledge of the subject this is, however, unattainable.

The methods made use of in dyeworks for ascertaining the quality of cochineal consist in making dyeing experiments on a small scale, and by comparing the effect of the decoction of a given sample with that of a standard specimen of cochineal, on pieces of mordanized cotton, woollen, or silk stuff. In this way not only the strength, but also, and what is often more important, the quality or tint of the colour contained in the sample can be ascertained.

*Distinction of the Cochineal Red from other similar Red Colours.*—An aqueous decoction of cochineal, although bearing a great similarity in its behaviour towards various re-agents with a solution of carminic acid, shows some deviations, which generally are ascribed to the presence of some nitrogenous substance still unknown.

LASSAIGNE asserts that the colouring matter contained in the kermes is identical with that of cochineal;

experimental proofs of this are however still wanting. On the other hand, it is stated that the tints produced with kermes are much less brilliant, although more stable and less readily acted upon by chemical reagents; also that cotton cannot be dyed with kermes.

The colouring matters of Lac dye and the other *Coccidæ* bear also a strong chemical resemblance to that of cochineal, but they also have as yet not been sufficiently examined to ascertain their true chemical nature.

The colouring matter of the red dye-woods, such as Brazil-wood, Sapan-wood, Peach-wood, &c., resembles in many respects that of cochineal, but the colours obtained from them are not nearly so rich, nor are they as stable. Chemically they may be readily distinguished by their calcium compound, which is of a violet colour and readily soluble in water, whilst that of cochineal-red is of a dark purple, almost black colour, and insoluble in water.

The application of cochineal in the arts is now almost entirely confined to the production of carmine and the brilliant scarlet dye on silk, and especially on wool. These colours have as yet not found a substitute amongst the numerous red-colouring matters derived from coal tar; none of these approach the peculiar and brilliant tint of carmine, or the scarlet on silk or wool obtainable from cochineal.

*Carmine.*—It is uncertain when this beautiful pigment was originally discovered, but as early as 1656 Homberg published a recipe for preparing it, and at that time it was already a well-known colour. According to Wiegleb,* it was accidentally discovered in Florence (or Pisa) by a Franciscan monk. In those days, and even up to recent times, cochineal was considered to possess some valuable medicinal properties, and it was during the process of preparing some medicament from it that the formation of carmine was first observed. Possibly its name is due to its original connection with some such medicinal preparation, and may have been derived from the Latin word *carmen* (carminative?); or by contraction from the Latin *carmesinus*, purple colour.

The true chemical nature of carmine is still only very imperfectly known. This is partly due to the secrecy which was observed with regard to the manufacturing processes, partly to the costliness of the material, and partly to inherent difficulties of the subject itself.

Carmine is prepared by treating a boiling aqueous decoction of cochineal with alum and a salt of an organic acid, such as bitartrate or binoxalate of potassium. It is essential that the vessel or boiler in which the operation is carried on is made of tin or well-tinned copper, otherwise the brilliancy of the resulting colour is much impaired. Formerly a mysterious influence was ascribed to the kind of weather or atmospheric condition, and it was stated on high authority that good carmine could only be prepared during a bright sunny day. On this account it was erroneously supposed that in England carmine could not be manufactured of the same brilliancy as on the Continent.

*According to an old German process*, 1 lb. of crushed cochineal is boiled in 1 gallon of water for a quarter of an hour, then 1 oz. of powdered alum is added, and the boiling continued for three minutes longer; after this the vessel is removed from the fire, allowed to stand for some time, and then the clear supernatant liquid is decanted into clean receptacles, which are set aside for several days, when about 1½ oz. of carmine is deposited. An additional half oz. of inferior quality is obtained by permitting the mother liquor again to repose for a length of time.

*According to a French method*, 1 lb. of crushed cochineal is boiled for fifteen minutes in 10 litres of distilled water, then 30 grms. of cream of tartar are added, and the boiling continued for ten minutes more, 15 grms. of alum are now added and again boiled for two minutes. The liquid is then allowed to settle, and as soon as clear is drawn off in flat glass or earthenware pans, in which the carmine deposits.

*Method of Alyon and Langlois.*—500 grms. of best crushed cochineal are boiled for twenty minutes with 7·6 grms. of carbonate of sodium in 15–20 litres of water; to this are then added 24 grms. of alum and 4 grms. of cream of tartar, and the liquid allowed to stand quiet until settled. The cochineal dregs fall to the bottom, and after a quarter of an hour the dark-red turbid liquid is poured through a silken sieve, and after a short while through another; the clear liquid is now thoroughly mixed with the fresh albumen of two eggs, and gradually warmed, when the carmine is deposited. By adding a second quantity of albumen to the supernatant liquid, and warming again, a further small quantity may be obtained, which, however, is of an inferior quality.

*Method of Madam Cenette of Amsterdam.*—2 lbs. of crushed cochineal, of the best quality, are boiled for two hours with 15 galls. of distilled water. Then 3 ozs. of pure nitrate of potassium are added, and in three minutes 4 ozs. of binoxalate of potassium. After having boiled for ten minutes more, the fire is removed and the liquid allowed to settle. The clear liquor is then decanted into shallow bell glasses and set aside for three weeks. At the end of this time the film of mould formed on the surface is carefully removed, without disturbing the liquid underneath, which is then drawn off by a syphon. The deposit of carmine left at the bottom of the vessels, when drained and dried in the shade, is of superior brilliancy and beauty.

[It will be noticed that in this latter method the use of alum is altogether omitted. Inasmuch however as carmine, according to our present knowledge of the subject, has to be considered as an alumina compound, it became desirable to ascertain whether carmine could actually be produced without alum; and accordingly this celebrated process, which for some time back has been copied from book to book, was put to the test. Several trials, in which the above description was followed as closely as possible, produced nothing but a rich crop of mould. It

* Joh. Chr. Wiegleb. Die natürliche Magie, vol. i. p. 242. Berlin and Stettin. 1782.

may be therefore assumed, that in communicating or transcribing this method the alum was intentionally or unintentionally omitted.—HUGO MÜLLER.]

Pure carmine forms an amorphous powder of an intense bright red colour, peculiar to this substance; the tint of which, according to its mode of preparation and its more or less dense condition, varies somewhat. Freshly prepared carmine, when examined under the microscope, appears in the form of irregular aggregations of spheric grains without any distinct sign of crystallization. Carmine is insoluble in water, alcohol, ether, benzol, the essential and fat oils. It is soluble in the stronger mineral acids, insoluble in acetic acid. In the alkalies and in ammonia it is perfectly soluble, forming a deep red or crimson solution. From the ammoniacal solution, when exposed to the air or saturated with acetic acid, the carmine is precipitated with its original properties. Carmine when brought in contact with solutions of the caustic alkaline earth, or the salts of the heavy metals, is more or less readily acted upon and deprived of its brilliant red colour. On dissolving carmine in dilute ammonia there is generally a small quantity of a whitish insoluble substance left behind, which consists of cochineal-wax and fat. Not unfrequently, however, carmine is adulterated with starch, vermilion, and similar substances, which may be readily detected by their insolubility in ammonia. It is otherwise with certain other admixtures, like albumen, casein, and gelatine, which are often added during the process of making the carmine, partly for the purpose of facilitating its precipitation, partly for the purpose of producing a light and flocculent carmine, which for many purposes is preferred on account of its softness and velvety brilliant colour. Pure carmine on being incinerated leaves about 12 per cent. of white ash, which consists of alumina and a little lime. Accordingly, this substance must be considered an alumina compound, most probably of one of the carminic acids; and it is a remarkable fact that alumina, in this combination, becomes soluble in ammonia. It may be mentioned in connection with this that all carminates, whatever their base may be, are soluble in ammonia, and like the carmine are precipitated when insoluble in water from such solution apparently unchanged on carefully saturating the ammonia with an acid.

The mother liquor from which the carmine has separated contains still a very considerable quantity of colouring matter, which may be utilized by neutralizing the liquid and adding freshly precipitated alumina, or by making the liquid alkaline and precipitating with a solution of alumina whilst hot. In this way a crimson-coloured precipitate is obtained which resembles carmin-lake.

The colouring matter retained in this mother liquor is not capable of being transformed into carmine, as might be supposed, by a further addition of alum or the other ingredients mentioned above, for these only will cause a slight precipitate of a crimson colour, but not of carmine. This behaviour obviously leads to the conclusion that one of the necessary elements for the formation of carmine is wanting, or that the colouring matter retained in the mother liquor is altogether different from that which enters into the composition of carmine, and therefore is incapable of forming this compound.

It follows from this that, in order to obtain the best possible result in making carmine, it is requisite to adjust the necessary quantities of the ingredients, and especially of the alum to be used, by previous experiments in accordance with the quality of the cochineal. If too little alum is added, the carmine separates with difficulty; if too much is used, the tint of the carmine is more of a crimson colour, and less brilliant.

*Carmin-lake* is of a crimson colour, and is produced by precipitating an alkaline decoction of cochineal with a solution of alum, or by treating a simple decoction of cochineal with fresh prepared hydrate of alumina.

*Cochineal Scarlet.*—This colour is now rarely prepared in the form of pigment, but its application as a dye for wool is of great importance, as its particularly bright and rich tint cannot be obtained by any other means. This colour is the tin compound of the cochineal red, and is obtained by the usual process of dyeing, solutions of the oxides of tin being employed as the mordant. The brightest shades of scarlet are produced by dyeing the wool or silk previously in a solution of annotta, and afterwards in a clear decoction of cochineal, mixed with cream of tartar and the so called "dyer's spirit," which is a mixture of bichloride and tetrachloride of tin. By using a decoction of cochineal in combination with alum and chloride of tin, without annotta, a crimson tint is obtained.

*Cochenille Ammoniacale.*—Before the introduction of the violet and purple aniline colours, various shades of violet and purple were obtained with this preparation, especially in the dyeworks of France. It used to be prepared in two forms, called *cochenille ammoniacale en tablette* and *en pâte*. The former was obtained by treating 1 part of powdered cochineal with 3 parts of liquid ammonia for four weeks in a well closed vessel, then adding 0·4 parts freshly precipitated alumina, evaporating the mixture in a copper vessel, and finally drying the residue with steam-heat. The latter was prepared in essentially the same manner, without the addition of alumina, and merely evaporating the resulting liquid to a certain concentration. SCHÜTZENBERGER,* who examined this dyeing material, ascertained that on leaving an ammoniacal solution of carminic acid for some time by itself, a peculiar change takes place, which appears to consist in the formation of a compound which contains nitrogen, and which may be considered to be an amide or amido-acid, derived from carminic acid. This carminamide differs from the salt-like derivations of carminic acid by its violet colour being not changed by acids, and by its precipitate with tetrachloride of tin not being of a scarlet but a dark crimson colour.

* SCHÜTZENBERGER, Comptes Rendus, vol. xlvi. p. 47; Ann. de Chim. et Physique, vol. liv. p. 52.

**COPPER.**—*Cuivre*, French; *kupfer*, German; *cuprum*, Latin. Symbol, Cu; atomic weight, 63·4. This metal has been known from the remotest times. It seems that in the earliest historic times it was extensively employed in the formation of domestic and martial implements, as well as for decorative purposes. *Bronze*, spoken of in the Bible as *brass*, is of very ancient origin. According to modern analysis it consists of copper, tin, and very small quantities of other metals, such as iron, nickel, cobalt, &c. Werner is of opinion that copper was the first of the metals discovered and extracted by man, both from the physical nature of its ores, and the facility with which it fuses. There is little doubt that the ores of copper were smelted; and, after the metal was obtained, it was subsequently alloyed with tin. The course adopted by the ancient metallurgists for extracting the metals is veiled in obscurity; but, as with most of the products of antiquity, it may be presumed to have been tedious, laborious, and imperfect, beyond the conceptions of those who are now engaged in the business.

The Syrians and Phœnicians were, as appears from various records and the quantity of bronze which they manufactured, large traders in copper; and doubtless, during the search of the latter people for tin in Great Britain and Ireland, they found considerable quantities of the metal. This is the more probable, from the circumstance of many bronze articles being lately discovered in some of the old workings in Cornwall attributed to that commercial people.

Copper seems to have derived its name from *Cyprus*, the island from which the Romans first procured their supply, and which, with Rhodes, continued for a considerable period to constitute the great emporium for the metal, somewhat resembling in this respect the Cornwall and Swansea of Great Britain. It was termed *æs cyprium*, which was shortened to *cyprium*, and ultimately changed to *cuprum*. The Greeks termed copper and bronze indifferently χαλκός.

In the middle ages roofs of houses were occasionally constructed of copper, or covered with it, and laws were usually engraved upon plates of this metal. In the alchemist's nomenclature copper was called *Venus*, not so much on account of the beauty of its lustre, it being accounted an imperfect metal, but from the facility with which it united to and was changed by other bodies.

In England the earlier copper works were situated in the northern counties; at Swansea (where now is the chief manufacture) they sprung up in the early part of last century. Towards the end of that century copper-smelting works existed also in Cornwall; but these were afterwards discontinued, and now the ores of Cornwall go to Swansea to be reduced.

Preparation of the Pure Metal.—This may be procured by passing dry hydrogen gas over pure oxide of copper, heated to redness in a tube of porcelain or hard German glass. The hydrogen unites with the oxygen of the oxide of copper, producing water, which escapes at the end of the tube. After vapour has ceased to condense upon a cold porcelain surface held to the aperture, the deoxidation is completed; the current of gas is to be maintained during the time the contents of the tube are cooling. The copper is now extracted in a finely-divided state, and may be melted into a globule.

Copper may likewise be obtained by putting 6 parts by weight of oxide of copper, and 1 part charcoal in powder, into a crucible, and subjecting it to a high heat; the metal is obtained as a small button at the bottom. Adding a little borax assists this result.

The pure metal can likewise be obtained from commercial copper, by dissolving it in nitric acid, and adding a little sulphuric acid to the liquid to render it slightly acid; a plate of iron is then immersed in the blue liquor, and the whole left to repose till the solution becomes colourless. The whole of the copper is by that time precipitated upon the plate of iron; it is collected, washed first with dilute sulphuric acid, to dissolve any particles of iron that may be adhering to it; then with water, to remove every trace of the acid; and, finally, dried and fused into a button. When prepared according to the first process, and the quantity of oxide is small, the metal appears in films, which by reflected light show the characteristic red of copper, but by transmitted light are beautifully green.

Physical and Chemical Characters.—Pure metallic copper has a fine red colour, and in this respect it differs from all the other metals, except titanium; it is capable of receiving a good polish; is malleable and ductile, and can be beaten out into very thin plates or drawn into very fine wires. Its melting point is 1200° C., Pouillet; 2204° Fahr. (1207° C.), Guyton Morveau; 2538° Fahr. (1398° C.), Daniell, showing that it is more fusible than gold, but less so than silver. Liquid copper expands on cooling: if the metal is contaminated with red oxide (dioxide of copper, $Cu_2O$) it melts at a lower temperature, and solidifies without expanding. In tenacity it ranks next to iron; a wire of the metal 0·787 of a line in diameter sustains a weight of 302·278 lbs., according to Guyton Morveau's experiments. The specific gravity of copper varies with its state of manufacture, from 8·89 to 8·95; the fused metal has a density of 8·89 to 8·91; uniguited copper wire, 8·93 to 8·94; ignited wire, 8·93; and flattened wire or sheet copper, 8·95. The hardness of this metal is not very great, it being scratched by calcareous spar. Its power of conducting heat is a little more than two and a half times that of iron; its specific heat in relation to that of water is as 0·095 to 1; and its linear expansion, when heated from 32° to 212° Fahr., as ascertained by Lavoisier and Laplace, is 0·000017; Troughton says, 0·000019.

During the time copper is kept in fusion it absorbs oxygen, if the fused metal be exposed to the atmosphere, whether in furnace or crucible. At a very high temperature it boils, and if it be exposed to the air in this state it emits fumes, which condense upon cold surfaces into small globules, the nucleus being

metallic, and the exterior coating oxide of copper. Exposed to dry air, the metal remains unchanged; but when moisture is present it becomes tarnished, and a coat of oxide and carbonate forms upon it. Heated to redness in an atmosphere of steam, no decomposition occurs; but at a white heat hydrogen is evolved, and oxide of copper formed. Finely-divided copper burns like tinder; and if the flame be intensified by a stream of oxygen gas, it takes fire, and burns with a beautiful green light.

Copper crystallizes in rhomboidal forms, when a large quantity of the metal is allowed to cool; but when precipitated by galvanic action upon a plate of iron, the crystals are octahedral. A dilute solution of a copper salt left in contact with wood often deposits cubical and octahedral crystals. The glittering spangles in the *aventurin glass* made some time ago at Murano, near Venice, and which was highly prized for decorative purposes, have been proved by Wöhler to consist of crystals of metallic copper.

Nitric acid dissolves copper, giving rise to a nitrate with disengagement of nitrogen dioxide, which, on coming in contact with air, is converted into nitrogen tetroxide; dilute sulphuric acid has no action upon it; but concentrated oil of vitriol, at a boiling temperature, forms with it sulphate of copper, a part of the acid being decomposed into oxygen, which unites with the metal, and sulphurous acid, which escapes.

Hydrochloric acid dissolves with difficulty compact masses of copper; but if they be finely divided, solution is effected with facility.

Copper is a dyad metal in its most stable salts, univalent in its cuprous compounds.

Ores of Copper.—These form a numerous class of minerals, the recognition and distinction of which is extremely important. Below is given a more or less detailed description of each of them, as well as of other minerals containing copper which have hitherto been met with in quantities too small to constitute them an *ore*, but which still should be known, as often pointing to the presence of the other minerals in larger quantities.

List of Copper Minerals.

| | General Composition. |
|---|---|
| * Native copper, | Metallic copper. |
| * Red copper, | Sub-oxide. |
| Chalcotrichite, | Do. |
| * Black copper, | Protoxide. |
| Tenorite, | Do. |
| * Malachite, | Carbonate. |
| Azurite, | Do. |
| Atacamite, | Oxy-chloride. |
| Cyanosite, | Sulphate. |
| Chrysocolla, | Silicate. |
| Dioptase, | Do. |
| Liebethanite, | Phosphate. |
| * Copper glance, | Sulphide. |
| * Purple copper, | Sulphide of copper and iron. |
| * Copper pyrites, | Do. |
| * Grey copper, | Sulphide of copper, antimony, and other metals. |
| * Bournonite, | Sulphide of copper, lead, and antimony. |
| Whitneyite, | Arsenide. |
| Copper mica, | Arseniate. |
| Oliverite, | Phospho-arseniate. |

* An asterisk marks those which at present supply copper in a large way.

*Native Copper.*—Copper is one of those metals which are found in nature in a metallic state. Native copper is thoroughly tough; it commonly occurs in thin plates, squeezed out as it were into dendritic forms; but at several places, especially round Lake Superior, thick masses of it have been discovered and raised. It occurs also in crystals of the cubical system. It is often associated with native silver. Its occurrence in the native form is accounted for by presuming that the sulphate of copper which would result from copper pyrites in the presence of moisture has been exposed to an electro-chemical action, by which the metal has been deposited. It has also been supposed to be formed by the deoxidation of cuprite.

*Red Copper* or *cuprite;* in French, *cuivre oxydulé;* in German, *kupferroth* or *rothkupfererz.* Composition, $Cu_2O$, having 88·8 per cent. of copper. It is chemically known as red oxide, or dioxide of copper. It has a blood-red or cochineal-red colour, and a lustre that varies from sub-metallic and adamantine to earthy; some specimens are partly transparent. It is brittle; the hardness from 3½ to 4, the streak being of a brownish red, and sometimes shining; the specific gravity is 6. It crystallizes in the cubical system, the usual form being the octahedron, with an octahedral cleavage. Before the blow-pipe it fuses, and on charcoal in the reducing flame may be reduced to the metallic state. Red copper occurs in most copper localities, though by no means often in any large quantity.

*Chalcotrichite.*—This mineral has the same composition as the last, and is of the same cochineal-red colour; but it belongs to a different crystalline system—the trimetric. It usually occurs in a fine capillary or fibrous form.

*Black Copper* or *Melaconite*; in French, *cuivre oxydé noir;* in German, *kupferschwartz.* Composition, CuO, being 79·8 per cent. of copper; but it commonly has impurities, both earthy and metallic, which lower the percentage. It is black in colour; occurs amorphous, sometimes in botryoidal masses, sometimes in a powdery state; the lustre may be either sub-metallic or earthy. Hardness of the less friable specimens, 3. Its behaviour before the blowpipe is similar to that of cuprite, first fusing, and then, with reducing agents, giving a globule of copper. It is not uncommonly found in copper mines, being doubtless a product of the decomposition of other copper minerals: near Lake Superior it has been raised in large quantities.

*Tenorite.*—This is a mineral of the same composition as the last (CuO). It occurs in small hexagonal crystals of a dark steel-grey colour. It is found in the craters and in the lava of Vesuvius, having been deposited from the vapour of the eruptions.

*Malachite*, or *Green Carbonate of Copper.*—This mineral first became known to the general public in 1851. In the Great Exhibition of that year exceedingly magnificent specimens of it, used for inlaying sideboards, cabinets, &c., were displayed in the Russian department. Its fine polish and varying depth of colour give an admirable effect in such work; later it became a great favourite

for such ornaments as bracelets, brooches, &c. Composition, $CuCO_3 + CuH_2O_2$, which would be of CuO 71·9, of $CO_2$ 19·9, of $H_2O$ 8·2; analyses give about 56 per cent. of copper.

The colour is bright green of various shades, which generally are in concentric bands; the streak is of a green paler than the colour. The lustre varies from adamantine or vitreous on the one hand down to earthy; it is sometimes translucent, more usually opaque. Hardness, 3½ to 4; specific gravity, 3·7 to 4. It crystallizes in the monoclinic system, but it more commonly occurs amorphous, in mamillated, stalagmitic, or in stalactitic forms. These, as well as the banded appearance before described, show how malachite has been deposited, namely, from a solution of copper from above, carbonic acid-bearing water having acquired the metal from other copper minerals and brought it down to be deposited in the rock cavities. Heated in a close tube it yields water and blackens; before the blowpipe on charcoal it fuses, and is reduced to metallic copper.

The chief localities for malachite are the Ural Mountains and South Australia, which latter country has afforded and is affording great quantities to the smelter.

*Azurite*, or *Blue Carbonate of Copper*, or *Chessylite*; in German, *kupferlazur*.—This, like the last mineral, is a hydrated carbonate of copper, but the proportions of the elements are somewhat different; its formula is $2(CuCO_3) + CuH_2O_2$, which gives of CuO 69·2, of $CO_2$ 25·6, and of $H_2O$ 5·2 per cent. The colour is bright blue, of a shade somewhat darker than azure; the lustre is vitreous; it has various degrees of transparency. It is brittle; the hardness varies from 3½ to 4¼; the streak is of a paler blue than the surface colour. Specific gravity, 3·5 to 3·8. It crystallizes in the monoclinic system. Before the blow-pipe azurite behaves like malachite. Azurite has been obtained in smelting quantities at Chessy in France, and, later, from South Australia; copper of a good quality resulted.

*Atacamite*.—Native oxychloride from Peru and Chili. Analyses give 15 to 16 per cent. of copper. This mineral is more or less translucent. Its colour is of various shades of green, and its streak apple-green; its lustre is from vitreous to adamantine. Hardness, 3 to 3½; specific gravity, 4 to 4·3; when crystallized it is found in forms belonging to the trimetric system. Before the blow-pipe it gives a blue tinge to the flame, and on charcoal gives a globule of copper. This mineral has only occasionally been worked as an ore of copper.

*Cyanosite*.—This is the native sulphate of copper, or blue vitriol; it is produced in nature by the oxidation of the sulphides.

*Chrysocolla*; in German, *kieselkupfer*.—Native silicate of copper; the percentage of copper varies from 45 down to 20 or less. This ore is of a turquoise-blue colour, inclining to green, sometimes translucent; the streak is white. Hardness, 2 to 3; specific gravity, 2 to 2·2. It does not crystallize, but is found massive or in crusts. Before the blow-pipe it is infusible, but with soda or charcoal gives a globule of copper.

*Dioptase* is another silicate with the elements in somewhat different proportions. It is of a vitreous lustre and translucent, of an emerald-green colour and green streak. Hardness, 5; specific gravity, 3·2. crystalline system, hexagonal. Before the blowpipe it acts as does chrysocolla.

*Liebethanite*.—This is a hydrous phosphate of copper; it is of resinous lustre and olive-green colour. Hardness, 4; specific gravity, 3·7. It crystallizes in the trimetric system.

*Copper Glance*, or *Red Ruthite*; in French, *cuivre sulfuré*; in German, *kupferglanz*. — Composition, $Cu_2S$, containing from 75 to 79 per cent. of copper. This is a very valuable ore on account of its richness in copper, but it is not so widely disseminated as other sulphur compounds of the metal to be noticed below. It has a metallic lustre and a dark grey colour, which is apt to change by tarnishing to an iridescent blue or green; the streak is the same as the original colour, and sometimes shining. Its hardness is 2½ to 3; the specific gravity 5·5 to 5·8. The crystalline forms are peculiar and recognizable; they are modified prisms of the trimetric system, often in twinned combinations, which are sometimes of a stellate arrangement. Before the blow-pipe it fuses, and on charcoal copper may be reduced from it.

*Purple Copper*.—This is also called erubescite and bornite. In French, *cuivre pyriteux hépatique panaché*; and in German, *Buntkupfererz*. Composition, $2Cu_2S + FeS$, the copper being about 60 per cent. of the whole. It is of a metallic lustre, and a colour which is somewhat brownish coppery red; usually its surface is varnished purple and blue; thes treak is greyish black, slightly shining. It has a hardness of 3, and a specific gravity which varies from 4·4 to 5. It crystallizes (though seldom) in the cubical system. Before the blowpipe it fuses to a magnetic globule. It commonly occurs in company with the other sulphur bearing ores of copper, and is often an important ore itself.

*Copper Pyrites*.—In French, *cuivre pyriteux*; and in German, *kupferkies*. Composition, $CuFeS_2$ or $Cu_2S,Fe_2S_3$, the copper being from 32 to 34 per cent. It is of a metallic lustre and a brass yellow colour, which, as in the case of the last mineral, though not so commonly, tarnishes and becomes iridescent. The streak is greenish black, a little shining. The hardness is from 3½ to 4, the specific gravity 4·1 to 4·3. It crystallizes in the pyramidal or dimetric system, in forms which closely resemble forms of the cubical system; it often takes hemihedral forms. Before the blowpipe it fuses to a magnetic globule, while with fluxes it easily yields a bead of the metal. This is the ore of copper most commonly met with in Britain, and indeed, taking the world over, the principal source of the metal.

*Grey Copper*, also called *tetrahedrite*.—In French, *cuivre gris*; in German, *fahlerz*. In composition it is a variable combination of sulphur with copper, antimony, arsenic, lead, silver, and other metals, the copper varying from 25 to 40 per cent. It has

a metallic lustre, and is of a steel-grey or iron-black colour. Hardness, 3 to 4½; the variableness of its composition telling upon this also. Specific gravity, 4·5 to 5·11. It crystallizes in the cubical system, generally in hemihedral forms, often twinned. Before the blowpipe it gives off antimonial and arsenical fumes, and with carbonate of soda yields metallic copper. As a source both of copper and of silver this mineral is of much value.

*Bournonite*, sometimes called by the Germans *radalerz*, is a sulph-antimonate of copper and lead. It contains 12·7 per cent. of copper. It is of metallic lustre, and a steel-grey colour; hardness, 2½ to 3; specific gravity, 5·7 to 5·9. It crystallizes in the rhombic system, the crystals often crossing each other in such a way as to give a radiated form to the mass, like the spokes of a wheel, with a cog-like circumference.

*Whitneyite* is an arsenide of copper, containing about 88 per cent. of copper and 11 of arsenic. It has a metallic lustre and reddish-white colour. Hardness, 3½; specific gravity, 8·4.

*Copper mica*, or *chalcophyllite*, a hydrous arseniate of copper. It is of vitreous or else a pearly lustre, and greenish colour. It crystallizes in the rhombohedral system in tabular crystals, with perfect cleavage of the basal plane.

*Olivenite*, sometimes called wood arsenite, is a hydrous arseniate and phosphate of copper. It is of adamantine or vitreous lustre and olive-green colour. Hardness, 3; specific gravity, 4·1 to 4·4. It crystallizes in the trimetric system.

These minerals, it must be understood, occur associated not only together, but also with various others, and especially with those non-metallic minerals which form what is called the *gangue* or vein-stuff that makes up the largest portion of the mineral vein. In copper-bearing lodes the most frequent of these minerals are quartz and fluor-spar, but quartz in general exceeds all the others in quantity. In mining, it becomes necessary to raise much of this *gangue* with the ores, so much indeed, that even after separating it as much as possible in the way to be described immediately, the percentage of copper in the ore that goes from Cornwall to the smelters is but from 5 to 7.

Mechanical Preparation of the Ores.—After the ores are extracted and brought to the surface, they are sorted, and are thus rendered more eligible to the purchaser for smelting.

The dressing to which the copper ores of Cornwall and Devon are subjected is mostly conducted in the following manner:—

*The first operation* is to separate the larger pieces of ore, called *spalling stuff*, which is for the most part of a good quality; the next batch is called *picking rough*, and is composed of lumps about the size of a cubic inch or more; it is removed by riddling the ore left, after selecting the large pieces, through a stout wire-gauze, the meshes of which are about three-quarters of an inch square; what passes through the riddle is denominated *shaft small*. Having done this, the spalling stuff is broken, either by flat-faced heavy hammers or by rollers, into pieces about the size of the second batch above mentioned, and assorted; pure pieces of ore, called *prills*, are obtained; and the other matters, which are again crushed with the *pickings*, are selected, and the better portions set aside with the prills of pure ore, which are ready for sale.

The remaining batches are now in great measure freed from gangue, by grinding, and afterwards washing with water, either in an inclined plane, or in a vessel with a wire-gauze bottom, in order to remove the foreign particles from the heavier metallic substances.

These processes are designated *jigging* or *buddling*, each of which promotes the desired effect, by causing the materials to deposit according to their relative specific gravity. When the most part of the impurities have been removed, and the ore is deemed sufficiently dressed for the smelter, it is made up into parcels or heaps ready for sale.

Copper-smelting at Swansea.—The process which will be described in detail under this heading is carried out to by far the largest extent in Swansea and its vicinity, a locality which surpasses any other in the world in the extent of its copper works. The same process is followed in Lancashire, and it has fairly been called the "English method" of copper smelting. To Swansea comes the ore which has been raised in Devon and Cornwall, as well as some that has been produced in Ireland, and large quantities of various ores from abroad.

Several circumstances have combined to render Swansea an emporium for copper—its comparative nearness to Cornwall and Devon, the great copper-mining counties; an easy approach for coasting and other vessels, by which material can be conveyed at a low rate; the adjacent coalfield to supply the works with that which is to them a first necessity, fuel; a return freight for coal to Cornwall for the mines, &c.

*Classification of the Ores.*—These vary both in percentage of metal and in composition, according as the supplies of them arrive from various countries. Of all it may be said that they are sure to be accompanied by a large amount of *gangue* (that is to say, non-metallic mineral substance—vein-stone), which is commonly silicious in composition. Five classes are distinguished by the smelter, which must be either differently treated or carefully mixed.

*First Class.*—Comparatively poor ores, containing copper pyrites and a considerable proportion of iron pyrites; in these the percentage of iron (from the two minerals) is of course large; copper is present to the extent of from 3 to 15 per cent.

*Second Class.*—Richer ores of like composition to that of the last class; they may contain from 15 to 25 per cent. of copper.

*Third Class.*—Copper pyrites chiefly, little of iron pyrites, but with some amount of other copper minerals, as of the oxidized ores.

*Fourth Class.*—Oxides and carbonates of copper, with little of the sulphides; the percentage of copper from 20 to 30.

*Fifth Class.*—A product of ores which have already undergone some metallurgical process, such as cal-

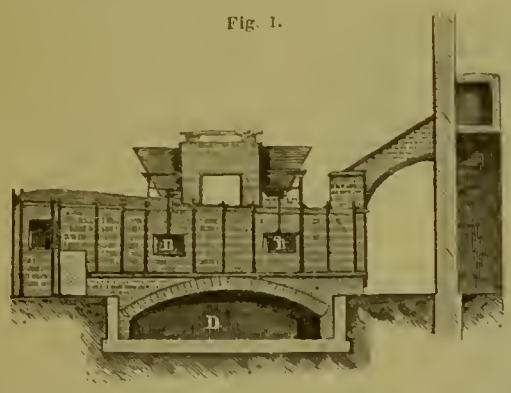
cination and fusion. It then constitutes a *regulus* or *matt*; rich in copper (yielding often as much as 50 per cent.), and free from earthy ingredients. It is imported from abroad for further smelting in England.

Ores of the first three classes are mixed for treatment, so as to contain from 8 to (at the most) 16 per cent. of copper. Those of the two last classes are brought in at stages of the process.

*General Sketch of the Processes.*—The reader should have a general idea of the chemical changes that take place in this somewhat elaborate system of metallurgy before loading his mind with the details.

The sulphurous and iron-bearing ores are first partially oxidized, the sulphides being turned partly into sulphates, partly into oxides; then they are melted down without any oxidizing influence, when there results a substance which is a sulphate of copper with some sulphide of iron, and above is a clay which consists of the earthy siliceous materials, combined with the rest (the greater part) of the iron. The mixed sulphide thus produced (which is called a regulus) is then roasted, so as to oxidize the remainder of the iron and get rid of the greater

Fig. 1.

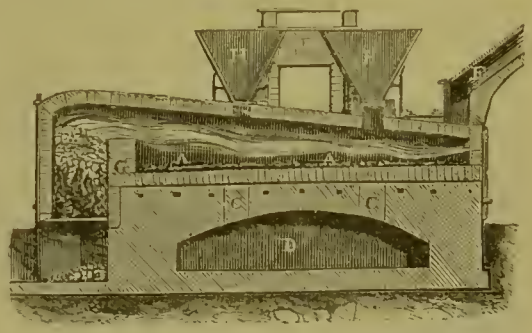



part of the sulphur. Then a second smelting is made, from which results a purer regulus than the first, and the percentage of copper is greatly increased. Then comes a process which consists in oxidizing the sulphur which was in combination with the copper, in doing which the copper is partly oxidized. Finally, there is a refining process (deoxidation) to get metallic copper in a marketable condition.

*First Process: Calcination of the Ores.*—This is carried out in a reverberatory furnace, of which Fig. 1 gives an elevation, Fig. 2 a section, and Fig. 3 a plan.

The bed, represented in the figures by A A, is of an elliptical form, truncated at the extremities of its greater axis. The walls, however, deviate from the elliptical outline near the openings, for the purpose of facilitating the removal of the charge. The furnace is constructed of firebricks set endwise in a bed of refractory fireclay; its length is about 16 feet and its breadth 13½. Beneath it is a vault, D, serving as a receptacle for the roasted material, which is drawn out by the furnace-men through the openings, C C, behind the working doors, B B. The arch of the furnace, the mean height of which is about 2 feet from the bed, contracts rapidly in height towards the flue holes, E, by which the gases evolved from the combustible products, both the fuel and the sulphur of the ore, pass off to the chimney. F is the fire-grate and G the bridge. Air is admitted into the furnace by means of openings, such as O, made near the fire, and capable of being closed at pleasure. The projections between the

Fig. 2.

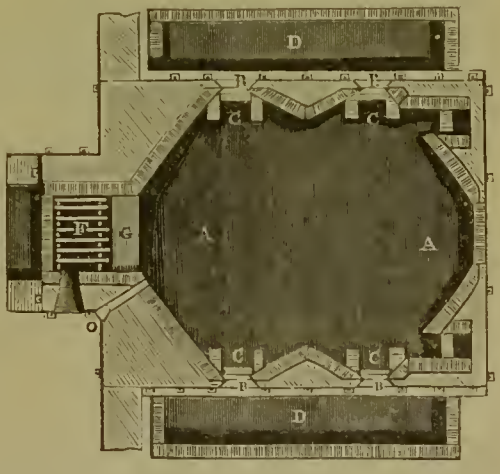



doors are intended to prevent accumulation of ore in places where the rake could not readily reach it.

In other forms of the furnace there is a channel made in the bridge, G, which opens outwardly, for the purpose of forming an equalized current over the whole of the hearth. On this account, and also because the current is heated in passing through the bridge, this construction is more effectual than the other.

H H are two large sheet-iron hoppers, with sliding

Fig. 3.



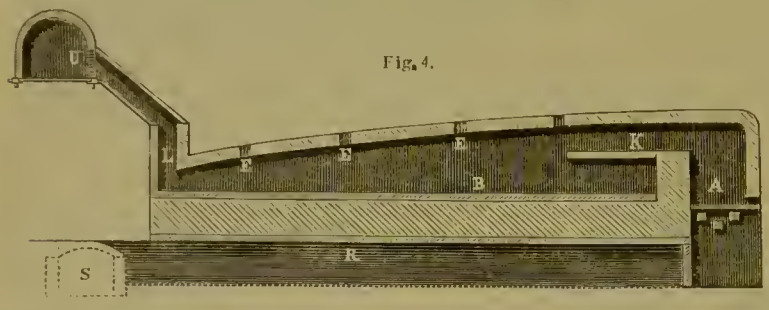

doors at the bottom; into these the ore to be roasted is put, and when required it is let into the furnace by drawing back the slides at the bottom. Exteriorly the furnace is bound with strong upright and horizontal bars of iron, to give it firmness.

Some furnaces are made longer in proportion than the one figured, having three, or even four openings on each side. Such a furnace is shown in Figs. 4 and 5: A is the furnace, the bars of which rest upon the topmost two of the transverse rods beneath it; the

lowest rod serves as a fulcrum for a crowbar in clinkering the fire; B is the hearth; C, square openings in the hearth through which the burnt ore is raked into the space, R, beneath the furnace. Over each of these openings is a door in the side (as in Figs. 1 and 3), through which the workman introduces his rake; the burnt ore is afterwards removed through the gate, S. The hoppers containing the raw ore are placed over the openings, E E E E, through which the charge is supplied as required. The raw ore is protected from the first fierce action of the flame by an arch, K, which extends across the furnace. The small flue, L, communicates with the main flue, U, leading to the chimney shaft.

The bars of the furnace, which are usually from 4½ to 5 feet in length and about 3 inches square, are placed at a considerable distance apart, and pieces of slag or bricks thrown upon them. Upon these the fire is made, and as the carbonaceous matter is consumed the earthy portion fuses and forms

Fig. 4.



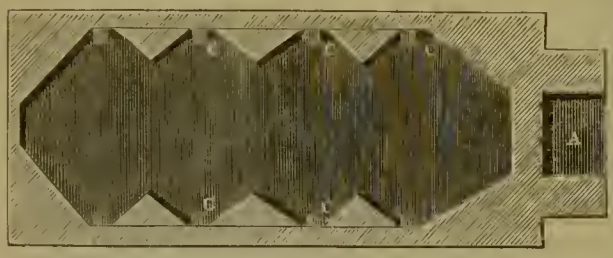
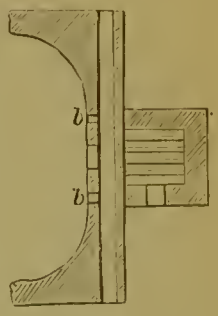




Fig. 5.

clinkers; but meeting the upward current of cold air it contracts, and numerous fractures sufficient for the passage of the current form in it. As this clinker accumulates the attendant removes a portion from the bottom, but retains a bed of from 12 to 18 inches in thickness upon the bars. By this means none of the coal is lost; the bars of the grate will serve for an almost indefinite period, as the mass of clinkers preserve them from burning, and the fire burns well. Openings or holes are made in the clinkers to give draught, and produce what is necessary in the roasting of the ore, namely, a sheet of flame over the hearth or bed. As the stream of air rushes through the grate and fire it is deprived of oxygen by the ignited coal, and the gases evolved over the bridge are nitrogen and carbonic oxide; scarcely any carbonic acid is produced during this part of the combustion. The air-holes represented in Fig. 3 now begin to act their part, for as the fresh stream of air rushes in through them, and meets with the half-consumed carbon at an elevated temperature, a fresh combustion takes place, the carbonic oxide takes fire, a flame is produced along the hearth of the furnace, and carbonic acid is formed.

Fig. 6.




But it must be remembered that not only is atmospheric oxygen wanted to consume the fuel and produce the necessary heat, a surplus also is required to oxidize the sulphurous ore. An ingenious plan adopted in some furnaces tends to effect this more completely; fig. 6 is a horizontal section of the fire-bridge; and shows a transverse channel through the bridge into which air flows from each end, and enters the furnace by the opening represented from *b* to *b*.

The furnace being already hot (for the action is kept up continuously) the charge, which generally amounts to about three or three and a half tons, is let into the furnace by removing the plates which cut off the communication between the hoppers and the interior. As soon as the whole is introduced the plates are again restored, and the ore spread evenly on the sole of the furnace by means of iron rakes working through the doors. This being done the doors are closed, the fire is replenished with the proper allowance of coal, and the draught through the clinkers established by abstracting a few of them if required, or loosening them by means of an iron rod made in the form of a pick at the end, the fire-door itself being closed.

The fire now begins to exert its influence upon the ore, but much care is required in its management; the object is to decompose sulphides as much as possible, and produce oxides instead. To effect this the temperature should not be too elevated, or the sulphides present will fuse and form a solid mass, offering only a small surface to the flame, and therefore rendering the roasting imperfect, and entailing much trouble besides, for the fused matt, as the sulphide is called, will adhere to the walls of the furnace.

The precaution of keeping the fire at a moderate working temperature is to be attentively observed during the first six or eight hours of the roasting, that is, as long as the ore contains an excess of sulphur and other volatile bodies; after this, to the end of the operation, the heat may be increased as the tendency of the charge to agglutinate becomes less. At first the aqueous vapours and some sulphurous acid are eliminated, the latter increasing in abundance during the first two hours, upon which the doors are opened, and a fresh surface presented to the flame by furrowing the charge in parallel lines

with a long iron tool, called a *rabble*. Then the fire is again charged, and the combustion of the ore allowed to proceed without interruption.

This work, rabbling the ore with rakes and bars, and of firing, takes place at the end of every two hours, till as much of the volatile products as can be expelled by the heat is driven off and oxygen substituted. This happens in from twelve to twenty-four hours; but towards the end of the calcination the fire is so urged, that when it is time to draw the charge the furnace is at its highest degree of heat. The doors are now opened, and iron plates which cover the openings, C C, Figs. 2 and 3, removed, in order that the calcined mass may be raked through them into the vault, D (or R, Fig. 4), whence, on cooling, it will be removed in barrows to undergo the ensuing process. This part of the operation is the most laborious and injurious to the health of the workmen, for, in addition to the great heat, they have to endure a worse evil in the shape of sulphurous and sulphuric, and often arsenious, acids, from the sulphur, &c., which was not expelled whilst the ore was in the furnace. The calcined ore should have a brownish black colour.

Immediately the calcined batch is cleared out, another is introduced and the evolution of aqueous vapours and sulphurous acid gas at once recommences. The material is spread out evenly, and after an interval of about fifteen minutes, during which the heat of the furnace will have fallen to the proper working pitch, the firing is renewed, and operations are again proceeded with as already recounted. Each furnace is watched by two men.

To save fuel the furnaces are now usually supplied with gas from one of SIEMENS' producers (see FUEL), and a fire bridge is placed at each end so that the flame can be sent either way by reversing the draught.

*Chemical Reactions of the First Process.*—M. LE PLAY gives the following numbers as representing the average result of the calcination: the first list is an analysis of the original or crude ore; the second, of the calcined ore:—

| | | Total weight. | Centesimal weight. |
|---|---|---|---|
| Crude Ore. | Oxide of copper isolated or combined, | 3·2 | ·374 |
| | Copper pyrites, | 194·2 | 22·710 |
| | Iron pyrites—bisulphide of iron, | 191·9 | 22·442 |
| | Various sulphides, | 8·7 | 1·091 |
| | Oxide of iron, | 5·2 | 0·608 |
| | Other oxides, | 2·3 | 0·269 |
| | Quartz and silica, | 294·4 | 34·428 |
| | Earthy bases, | 16·0 | 1·871 |
| | Water and carbonic acid in combination, | 4·2 | 0·491 |
| | Oxygen consumed, | 135·0 | 15·806 |
| | *Products:*— | 855·1 | 100·000 |
| Calcined Ore. | Oxide of copper, | 46·2 | 5·401 |
| | Copper pyrites, | 96·0 | 11·228 |
| | Bisulphide of iron, | 95·8 | 11·226 |
| | Other sulphides, | 5 2 | 0·600 |
| | Ferric oxide, | 100·2 | 11·718 |
| | Other oxides, | 5·2 | 0·608 |
| | Sulphuric acid in combination, | 9·5 | 1·108 |
| | Quartz and silica, | 294·4 | 34·408 |
| | Earthy bases, | 16·0 | 1·874 |
| Gaseous products, | Sulphurous acid, | 182·5 | 21·338 |
| | Water and carbonic acid, | 4·2 | 0·491 |
| | | 855·1 | 100·000 |

The ore does not lose much in weight, the quantity of oxygen absorbed in great part making up for the diminution of the sulphur; of the sulphur itself about half is evolved. It appears, then, that the chief change is a decomposition of a considerable portion of the copper and iron pyrites, and a consequent formation of oxide of iron, and of a less proportion of oxide of copper. This change, however, is not made at one step; it would seem that *sulphates* of the two metals are first formed, which, by a continuance of the heat, are made to lose their sulphuric acid. The oxide of copper spoken of as resulting is the suboxide; of the iron oxide, the greater part is sesquioxide, but Dr. PERCY has proved the presence of magnetic oxide as well.

The volatile results of the roasting in the calcining furnace are therefore:—

Aqueous vapour
Sulphurous acid,
Sulphuric acid,
Arsenious acid and arsenical vapours,
Fluoride of silicon and other volatile compounds of fluorine,
Solid matter, mechanically conveyed by the draught into the flue,
Carbonic acid, &c.

All these arise from the combustion of the fuel and ore; the water is formed by the oxidation of the hydrogen of the coal, as well as by the expulsion of the moisture in the mass. It is this which, acting on the sulphurous acid arising from the sulphur in the presence of the oxygen in the furnace, gives rise to sulphuric acid. The arsenic and its compounds are contained in the ore, and are expelled as such; but the former undergoes combustion in part, and forms arsenious acid. By the action of the silicious gangue upon the fluoride of calcium, fluoride of silicon is produced. Hydrofluoric acid is also generated, as is evidenced by the action of the gases upon glass. DUMAS accounts for its occurrence by the supposition that fluoride of arsenic is formed, which, in contact with the vapour of water, becomes converted into arsenious and hydrofluoric acids.

All these vapours pass off into the atmosphere, and from their enormous quantity, and their destructive influence upon vegetation, cause serious damage to the surrounding district. The constant evolution into the air of such immense volumes of poisonous gases must also be hurtful to animals. The face of nature in the vale of Swansea bears indelible traces of the ravages of the vapours. It is also to be regretted that such a vast quantity of sulphur should thus be wasted. Many exertions have been made to condense the poisonous fumes, in order both to prevent nuisances and to utilize the valuable products. The following is the plan adopted by SPENCE with considerable success:

In his first arrangement (Figs. 7 and 8) the calciner had a flat bed, A, for the ore, 40 feet long by from 6 to 9 feet in breadth; beneath this bed the flues, B, from the fire, C, traverse the whole length of the furnace, finally making their exit to the chimney shaft at D. The ore is supplied to the furnace by the hopper, E, and after parting with most of its

sulphur is transferred by slices towards the fire-end of the roaster, and a fresh charge is introduced; by the time it reaches the far end of the furnace it is thoroughly calcined, and is drawn out into an iron truck. Sufficient air to convert the sulphur into sulphurous acid is admitted at this end. The sulphurous acid gas passes into the vitriol chamber by the flue, F.

Fig. 9 is a modified form of the same furnace. Here the calcining furnace and the smelting furnace are combined. As the ore which leaves the calciner at a red heat is so far ready for smelting, and at the same time the waste heat of the smelting furnace is sufficient to effect calcination, much fuel is saved by joining the two furnaces.

K is the door of the smelting furnace; B B the flue conveying the waste heat under the calcining bed, A A; it passes by C into the shaft. The raw ore is supplied from the hopper, E; after being burnt it drops into the smelting furnace through the tunnel,

Fig. 7.

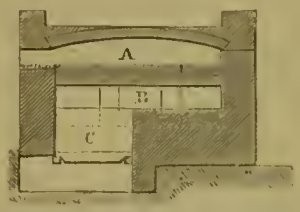
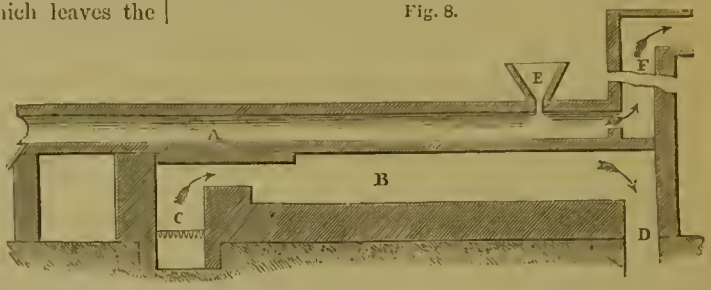



Fig. 8.

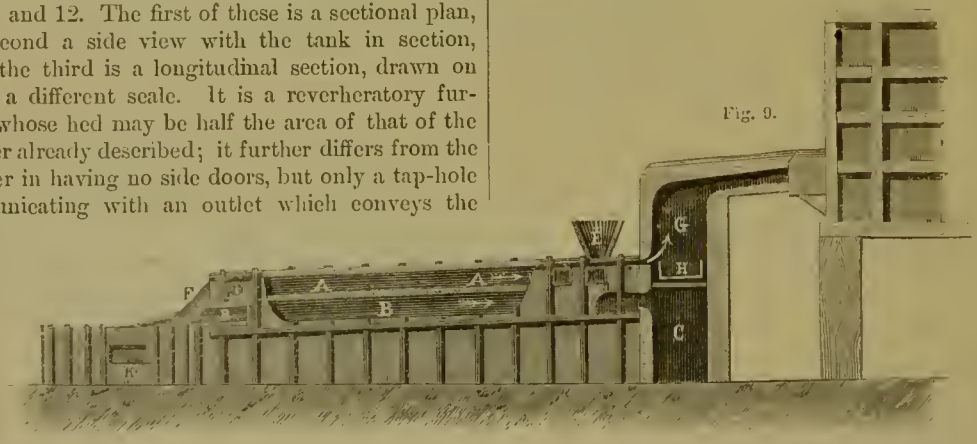



F. The sulphurous acid is conveyed by G over the nitre pot, H, into the vitriol chamber, I.

*Second Process: Melting of the Calcined Ore.*—The calcined ore is next melted with the slag from the *fourth process* (presently to be described), which slag is called *metal slag*.

The furnace employed is represented in figures 10, 11, and 12. The first of these is a sectional plan, the second a side view with the tank in section, while the third is a longitudinal section, drawn on rather a different scale. It is a reverberatory furnace, whose bed may be half the area of that of the calciner already described; it further differs from the calciner in having no side doors, but only a tap-hole communicating with an outlet which conveys the melted product into a proper recipient. In the following description the letters refer to the first two figures only, figs. 5 and 6. A is the bed or hearth where the charge is elaborated; this inclines towards the outlet already mentioned, so as to form a kind of basin: the bed is formed of alternate layers of sand and

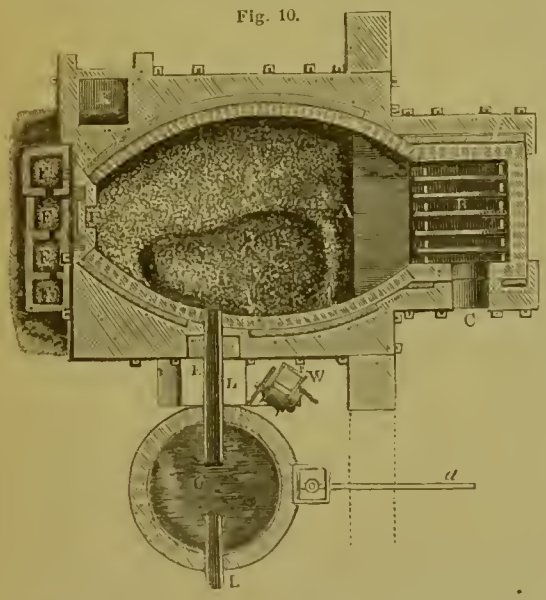
Fig. 9.




*metal slag*; B shows the furnace bars (which cover a much greater proportional area than do those of the calcining furnace), C, the fire-door, while the working door of the furnace is opposite to the fire. E is the door of the outlet, but this is securely closed during the period of working the charge. F, F, F are sand moulds, into which the slag is raked out; H, in the side view, is the hopper through which the calcined ore is introduced, the materials constituting the succeeding charge being put there whilst one is being worked off; G is a tank kept full of cold water by a supply-pipe, *a*, and emptied by another leading from it at the bottom. In this tank a frame of wood or iron is immersed, the bottom of which is composed of a stout wire gauze, the whole being connected by ropes or chains to a winch, W, which serves to lift the frame out of the tank when necessary. K denotes the chimney, which exercises a greater influence upon this than the preceding furnace. This is necessary, because the heat required in this second operation is much higher than in the first. The fire is constructed upon a mass of clinkers. The charge for this furnace consists of about 21 cwts. calcined ore, and sometimes fresh ore, of the sort that contains less sulphide of iron (of the third class), is added; sometimes larger furnaces and greater quantitities are employed. All this is introduced through the hopper; *metal slag* to the extent of 3 or 4 cwts. is added through the door at the end; the object of this last is two-fold—to render the whole more fusible, and to obtain the copper remaining in that slag. The man attending the furnace fills the hopper during the fusing of the charge, and has all the materials ready, so that when the furnace is tapped, a new charge is instantly let in, that no heat be lost. As soon as the charge from the

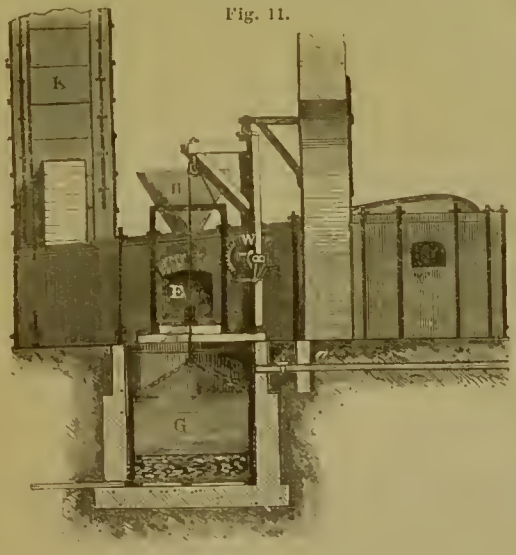
hopper is introduced into the furnace, the attendant spreads it as quickly as possible upon the bed or hearth, and then throws in interspersedly the pieces of slag. When all has been added the door is carefully closed and made secure by luting, as also the side opening; the furnace-man then replenishes the

Fig. 10.



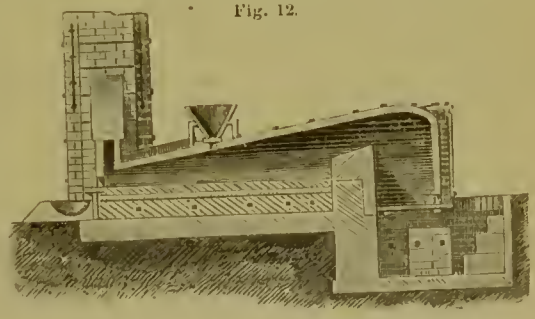

fire, and refreshes the draught by removing some of the clinkers, and opening the crevices with the pointed iron. The charge is unmolested for three hours and a half, the interior being observed from time to time, to watch the fusion. Fresh fuel is thrown on at the end of an hour and a quarter, or

Fig. 11.




less, as deemed requisite; the quantity being proportioned to the allowance for the working of each charge. In half an hour after the spreading of the ore on the hearth of the furnace the slag begins to fuse, and in a very short time it forms liquid channels, or little lakes, in the mass. Soon after, the fused mass extends over the whole hearth, from the combination of the iron and silica present into a very fusible silicate of iron. As the quantity of liquid matter increases, it becomes agitated from the evolution of sulphurous acid, produced by the oxidation of the sulphide of iron, a silicate of iron being formed instead. Fluoride of calcium also brings about the fusion more readily, and the decomposition of this compound in the presence of silica, by which fluosilicic acid gas is disengaged, favours the intimate mixture of the materials, and aids in the expulsion of the arsenic. At the end of about five hours the whole of the charge is melted, except those portions of slag which may remain at the sides of the furnace, and gas ceases to be evolved. The furnace-man now opens the door, and by a long rake rabbles the whole charge, by which means the unmelted portions are brought into contact with the fused mass, and thereby dissolved. He now urges the fire to its highest heat, which is maintained in that state for about half an hour. During this time the moulds for the slag are being prepared by spreading the sand evenly, and then digging out a form of a mould. Then the slag is raked out through the end door into these moulds. When this is done the process of charging and melting is repeated, and so

Fig. 12.



on until, after a lapse perhaps of twenty-four hours, enough of regulus has accumulated to fill the bed. Then the tap-hole is carefully opened to draw off the fused matt or regulus, which flows into the water tank, and in doing so becomes granulated; afterwards the box G, into which it had fallen, is raised by the winch, and the granulated substance is removed. In some works granulation is omitted and the regulus is run into moulds.

Some regulus is attached to the slag in the first of the sand moulds; this is carefully separated; a little also remains in the form of buttons with the mass of the slag, but if the operation has been conducted with care the loss is not great. The amount depends on whether the slag has been kept (by judiciously proportioning the supply of *metal slag*) to the proper consistency; for if it be too thick beads of regulus will remain in it, if it be too thin some of the regulus will be drawn out with it in the skimming. The products, then, of this second process are a regulus of sulphide of copper with some sulphide of iron, called *coarse metal*, having about 35 per cent of copper, and the slag, called *ore-furnace* slag. This slag is thrown away, and it is the only product of the whole series of operations which is entirely lost; the loss, by copper contained in it,

should be but small, but still it is appreciable, for in most of the refuse masses small globules of the copper sulphide can be seen. Mountains of discarded slag may be seen accumulated near some of the large smelting-houses, and conveyed from the works by rail and steam, at a cost to some of the large works of from £3000 to £5000 annually. Great quantities are used for roads and walls.

Every furnace is looked after by two men, each attending twelve hours, and the operations never cease night or day during the week till Sunday, from which time till Monday morning following all the furnaces remain uncharged. They are not, however, allowed to cool, but one or two men maintain the fires, so that they may be ready to receive a charge as the first thing requiring to be done at the beginning of the week. The night-shift is taken by the men alternately. To those who have been working at these furnaces for some time very few directions need to be given, so long as the ore operated upon remains of a uniform composition, as well in metal as in slag, for they have in that case only to add the proper quantity of fluxing matter at once, and proceed as just detailed; but any alteration in the nature of the ore, whether it be in the quantity of metals or in the amount of gangue, causes a derangement, which must be righted by a complete quantitative analysis of the ore.

When poor and rich ores are at hand, the easiest course, and that which is usually adopted, is to mix them in quantities calculated to produce a compound of the same mean composition as that which is generally operated upon; but if the materials cannot be thus regulated, the flux must be apportioned to produce the desired effect. Much care is taken to avoid having an excess of scoria, lest too much copper should be mechanically retained by it, and a loss sustained. For this reason fluoride of calcium is not used, except it is considered that the gangue is difficultly fusible; and the fused scoriæ from the succeeding operations are not on these occasions added at once, but only in successive small portions at a time, followed by a rabbling, till the whole contents have arrived at the desired fluidity. Having acquired this knowledge in the first charge, the proper fluxing materials are afterwards added at once, as long as the same class of ore is to be worked.

The chemical metamorphoses going on within the furnace are few and simple—merely the formation of a silicate of iron, and the consequent evolution of sulphurous acid and sulphur, with a few other changes. It nearly always happens that sufficient silica is present in the ores, at least in those raised in England, to take up all the iron; but when this is not the case a proportionate quantity of quartz sand is added. Oxide of iron manifests a great affinity for silicic acid at a high temperature, and combines with it, under this circumstance, in preference to any other volatile acid; hence the iron present in the ore in the state of sulphide, or rather in the calcined ore in the state of either oxide or sulphide, is converted into silicate of iron. It is necessary, however, to bring the substances into a very intimate contact before this combination can be induced, and hence the reason for adding a fusible flux. Silicate of iron already formed and fluor spar are the best suited for the smelter, as they readily fuse and form a bath in which the combination of the iron and the silica is effected. A commotion is caused by the evolution of sulphurous acid which greatly favours the chemical action; and in cases where fluor spar is employed this is maintained after the sulphurous acid ceases to be evolved.

The manner in which the fluor spar, or calcium fluoride, acts, is by parting with its fluorine to the silica, which should be present in excess, thus giving rise to gaseous silicium fluoride, the lime being oxidized. The most important part of the decomposition, however, rests upon the union of the iron and the silica.

The matt or regulus is a brittle substance of uneven fracture and semi-metallic bronze lustre.

*Third Process: Calcination of the Coarse Metal.*—If the coarse metal has been run into moulds, the cakes are broken up and heated with free access of air in a melting furnace. The matt which has been granulated is taken from the tank, dried, weighed, and conveyed to the furnaces, where it is to undergo the third process. These furnaces resemble in size and outline those devoted to the calcination of the crude ore, and the charge of matt is, as in the former case, about 3½ tons. This quantity is thrown into the hopper surmounting the dome of the furnace, and let down into the bed in the usual way by drawing the slide, and afterwards spread out upon the sole in the same manner as was done with the crude ore. The same purpose is here intended as in calcining the crude ore, namely, the expulsion of the sulphur, and the production of oxidized bodies; but as the chief part of the gangue is removed in the preparation of the matt, these results will now be much more effectually produced than when all the impurities were present. Great attention must here be given to maintaining the heat of the fire within bounds, so as to keep the material at just such a state of ignition as will facilitate the expulsion of the sulphur, but will be insufficient to fuse the mass, which would prevent its oxidation in an effective manner. On the whole, the heat is much higher in this than in the first operation, more especially towards the end of the roasting, which occupies about twenty-four hours. For this purpose 21 cwts. of coal are required, or three and a half quarters of a cwt. per hour. During the first two hours the fire is kept low, and then as the sulphur becomes eliminated it is increased regularly, so that in the course of about twelve hours the ore has attained an incipient red heat. At the end of eighteen hours the whole of the interior of the furnace should be at a cherry-red heat; and at the close of the operation the temperature of the whole should have assumed a bright redness. Every two hours the action of the fire is accelerated by a rabbling of the charge, by which a fresh surface is exposed to the flame, and the sulphur compounds become decomposed. Much importance is attached to the proper calcination of the matt in this operation, and, therefore, it is not left to the discretion of

the furnace-men; inspectors are appointed to attend each set of furnaces, and see that the work is duly attended to in every particular, especially the rabbling, which takes place at an interval of every two hours. If this be neglected, the whole of the sulphur will not be expelled in the form of sulphurous and sulphuric acids. Too high a temperature is less to be feared than too low a one, because the tendency of the ore to form masses will check the furnace-man's inattention in this respect, as he would have to break them up afterwards—a very laborious operation. When too little heat is applied, there is little danger of the charge agglutinating, and the rabbling is easily performed; but this is at the risk of not expelling the sulphur.

The change produced by the third roasting is expressed in the annexed table, which shows the relative weight of materials taken:—

| | |
|---|---|
| Coarse metal, | 0·804 |
| Oxygen derived from the atmosphere, | 0·196 |
| | 1·000 |

The products obtained by calcination are:—

| | |
|---|---|
| Calcined coarse metal for the succeeding operations, | 0·783 |
| Sulphurous acid and sulphuric acid, | 0·217 |
| | 1·000 |

The physical appearance, as well as the chemical composition of the matt, has altered; it suffers a diminution in bulk, and assumes a black hue. Throughout, the mass is friable, but where the grains are large and more solid, the exterior parts are easily reduced to powder, and the interior nucleus is hard and compact. After the whole charge is properly calcined, it is raked out through openings immediately inside the working doors, and falls through into a chamber under the hearth. This is called *calcined coarse metal*, and is, as soon as convenient, submitted to the next process.

*Fourth Process: Fusion of the Calcined Coarse Metal.*—It must be first noted that to the above product of the third process are now added the slags from some of the later processes, and other materials that may be enumerated below, and all is now melted down together.

The procedure in this stage of the work is analogous to the fusion for *matt* in the second process. It has for its object the removal of the iron, and the production of pure sulphide of copper, or at least as rich a compound as possible. The furnace used is of the same form as the melting furnace of the second process, except that there is no hollow in the hearth, but a gentle slope towards that side in which is the tap-hole by which the fused material is run out.

The material acted upon may consist of *granulated coarse metal* (to the extent of something more than one-half of the whole charge), *roaster slag* from the fifth process, *refining slag* from the sixth process, fresh ore of the fourth class, that is, rich ores with more oxide than sulphide, and without iron, besides copper scale and furnace waste.

Although the work in this process is simple, yet it is more difficult of management than any other yet described. The chief point to be attained is the blending of the calcined matt and the crude ore already mentioned, in such a way that the oxide of copper in the whole may be converted into sulphide by the impurities or sulphide of iron in the latter. It becomes a difficult matter to apportion the different materials. The whole charge being from 2 to 2½ tons, the percentage, on an average, may be represented as follows:—

| | |
|---|---|
| Calcined coarse metal, | 56 |
| Crude ores, | 24 |
| Slags from later operations, | 10 |
| Copper-scale, furnace-waste, and earthy matter, | 10 |
| | 100 |

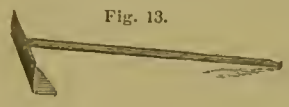
But these proportions should be made to vary according to the character of the ore and the slags. The only criterion which workmen have for their guidance is deduced from their observation on the first charge of a batch of these products. Practically the best decomposition is obtained, taking all allowances for the inequality of the oxygen and sulphur compounds into consideration, when the fusion is prolonged; and it has also been found that a better yield in quality, as well as in quantity, is ultimately produced when from 4 to 8 per cent of iron are retained in the matt, and from 3 to 5 per cent. of copper pass off in the slag. This slag forms a very important article in the operations of the smelting house, as it contains a very large quantity of oxide of iron, having generally about 50 per cent. of protoxide of iron, and about 3 per cent. of oxide of copper, combined with silica, which, when added to the calcined ores in the first fusion, forms a most excellent flux for the ore, which otherwise would require extra calcining, or addition of a flux of lime or fluor spar, which would add much to the cost of the operation. The enriching of the slags with oxide of copper is not an inconvenience in the work; nor is any loss suffered in consequence, but a saving, as all the slags produced in this, as in other processes, are fused in the second operation, and the copper in them recovered in the matt, which it improves and enriches. Should, however, too much oxide of copper be permitted to remain in the slag, it would react upon the sulphide of copper, and reduce a portion of it to the metallic state. When this happens, the metal is usually of a bad quality. Indeed, it is the chief aim of the furnace-man to prevent this; dividing his attention, however, with the production of the purest white metal that is possible under the circumstances.

The materials, in the proportion indicated in the table already given, or in such quantities as the judgment of the furnace-man suggests, are introduced through the hopper, and spread out in the usual manner; the larger portions, especially the scoriæ, are thrown in at the working door, and distributed evenly over the surface of the charge.

When this is done, the doors are closed, and then luted, and the fire regulated to enable it to give out

the required heat. At the expiration of an hour incipient symptoms of fusion appear, as well in the softening of the mass as in the evolution of the gaseous matter; the fusion of the whole progresses gradually till about three hours after charging, when it appears in two layers, the one as yet undissolved, floating on the fluid portion. All the volatile bodies evolved during the fusion rise from the double decomposition which takes place in the melted matter, but at the above period these are not disengaged in such abundance as to generate an effervescence in the mass. In about four hours after the charging the matters adhering to the sides of the furnace are struck into the bath, and the whole rabbled with an iron tool of the form shown in Fig. 13. At this period the flux, or scoria, is very fluid, and in a very short time, when the heat is increased, the whole mass is in tranquil fusion. The entire operation is completed in about six hours after the charge has been introduced. The furnace-door is then opened, and the attendant, by means of a long rake, skims off the scoriæ or slag; generally the bed for the slag has partitions, by which it is formed into pigs, or ingots, and these are removed and examined with greater facility than when in one mass. The tap-hole being now carefully opened, the very fluid matt, which at this stage has nearly attained to a white heat, flows out either into the cistern to be granulated, or it is conducted into channels in sand, where it is cast into pigs of about 1 cwt. each.

Fig. 13.



This is either *blue metal* or *white metal*, according to the amount of decomposition that has gone on. "White metal" contains about 75 per cent. of copper; it is an almost pure sulphide of the metal ($Cu_2S$), and is free from metallic copper. "Blue metal" contains about 56 per cent. of copper, 16 of iron, a large proportion of sulphur, and is usually vesicular with threads of copper projecting into the cavities. The slag is the *metal slag* treated in the second process.

*Fifth Process: Roasting the Blue or White Metal.*—The above regulus is now melted *with access of air*. This is done in a furnace like that wherein the former melting processes were effected, but having a side and an end door, and side openings for the admission of air. From 3 to 3½ tons of the regulus are introduced in large masses by the side door, and piled upon the floor of the furnace. The fusion is effected in about six hours; at this stage slag is skimmed off; then the heat is continued for several hours, during which time oxidation of the sulphur combined with the copper takes place, the melted material being as it were in a simmering condition from the escape of sulphurous acid gas. After a time the temperature is allowed to become so much lower that the surface begins to solidify; again the temperature is raised, and more oxidation goes on, till, after about twenty-four hours, it is thought that the process has gone sufficiently far, when the tap-hole is opened, by which the metal flows out into rectangular moulds formed in the floor of the foundry. This is called *blister copper*, on account of its numerous bubbles. The scoria (which was first skimmed off at a comparatively early stage, and lastly run into moulds just before tapping) bears the name of *roaster slag;* it is composed of silica, combined with the oxide of iron (FeO?) and some oxide of copper ($Cu_2O$?) from the regulus, and about 2 per cent. of sulphur; it is this that is added to the charge in the *fourth process*. The composition of blister copper is very constant, averaging from 93 to 96 per cent. of copper, with a little sulphur and oxygen, the latter being in all probability combined with the copper in the form of suboxide, which compound was *dissolved* by the metallic copper. The following may be considered a fair specimen of good blistered copper:—

| | |
|---|---|
| Copper, | 95·60 |
| Sulphur, | ·69 |
| Iron, | ·28 |
| Silica, | ·12 |
| Antimony, | trace. |
| Oxygen and loss, | 3·31 |
| | 100·00 |

The reaction taking place in the above process is explained by Dr. Percy as a formation of oxide of copper on the first slow melting of the mass, then, as it fell, an interchange with undecomposed sulphide, by which sulphurous acid and metallic copper resulted.

The advantage of checking the heat and afterwards raising it consists in this, that on the partial cooling the surface bursts out into volcano-like protuberances that afford a larger surface for further oxidation; the last raising of the temperature then mixes the later formed oxide, and causes a further reaction of the kind above described, so that nearly all the sulphur becomes expelled, the oxidation being at the same time so far carried to excess that some of the copper is oxidized, and qualities are produced in the metal which have to be corrected by the next process.

Blister copper contains about 95 per cent. of copper, together with small quantities of iron, sulphur, tin, antimony, &c. It is brittle, and has a deep red colour. It cannot be used in the arts on account of its want of tenacity.

*Sixth Process: Refining the Blister Copper.*—In this the toughening and refining of the copper, so as to bring it to a fit state for the market, are performed by a method similar in some respects to the preceding operation.

A charge of the pigs of blistered copper, weighing from 8 to 10 tons, is introduced by means of a peel into a furnace of the same construction as that used in the last operation, except that the grate is larger on account of the increased consumption of fuel required to maintain the proper heat, and that the hollow of the bed is towards the far end. Siemens' regenerative furnace is much used. The only additions to the metal till the preliminary roasting is completed are the adhering sand and part of the matt of the furnace; these are subsequently thrown off as scoriæ. Care is taken in the introduction of the masses of metal to place them so that the greatest amount of

surface shall be presented to the flame, and likewise that the draught may not be impeded. This being done the fire is attended to, and the heat sustained during the eighteen hours that the charge is left to roast. This is so managed that, in about six hours after the charging, the copper begins to melt freely, and the heat continuing to increase regularly, brings the whole, within the period of eighteen hours, to such a state that the oxides of any foreign bodies, together with some oxide of copper, will unite with the silica. What remains of the iron, or any other metal, in the molten bath, unoxidized by the current of air passing through the furnace, is oxidized by means of the oxide of copper, which is thus decomposed into metal and oxygen. The high temperature is maintained during a further period of three and a half or four hours, which renders the bath of metal as free from impurities as is possible under the circumstances. The working door is now opened, and the bath is found covered with a layer of scoria which is raked off, leaving the metal in the state that is called *dry*, that is to say, brittle, from the presence of diffused suboxide of copper (cuprous oxide, $Cu_2O$).

The second part of the process now commences. Hitherto one man had the care of two furnaces, but now more men are employed, and the preceding part of the business is so regulated that each furnace will be ready at the usual working hour in the morning. At this stage the metal is brittle, of a deep red colour, and coarse fracture; tenacity is to be acquired, as well by removing the oxygen as by causing a different aggregation of the molecules of the metal. The first thing which the refiner has to learn is the state of the *dry* copper, as it is called, and this is done by taking out a sample with a small ladle and casting it in a mould; when cold this is broken, and from its appearance, together with the state of fusion and the intensity of the fire, he calculates the quantity of charcoal, wood, or of coal, which will be requisite to communicate the suitable degree of toughness.

Ground charcoal, or the best anthracite coal, is scattered over the surface of the metal, and serves both to exclude the air and to deoxidize those portions of the metal in contact with it.

This constitutes the first step, but the action of the carbonaceous covering thus used cannot penetrate beyond the surface, and hence the oxygen in the interior remains unacted upon by it. To expel this it has been the practice, time out of mind, to agitate the fluid metal with a spar or pole of green wood, either birch or oak, and this continues at the present time to be the only method in use. One of these poles is thrust into the fluid bath, and the carbonaceous gases which it evolves effectually reduce, during their ascent through the fluid metal, any oxide of copper, carbonic acid being evolved. The two gases throw the metal into violent commotion, which serves to bring every particle of the red oxide of copper within the range of the deoxidizing agents. The ebullition of the metal by the action of the poles is continued from fifteen to about twenty-five minutes or half an hour, the surface being still kept covered by fresh additions of charcoal or coal. The period for arresting the poling is ascertained by taking samples from time to time, and testing their ductility and malleability in the vice and under the hammer. For this purpose the refiner has a small ingot mould attached to the end of an iron rod, and this he quickly dips into a spot at some distance within the door, from which he has cleared away the coal and scoria. When the sample solidifies, it is cut half through by a chisel or shears, and then repeatedly bent by blows from a hammer whilst it is held in the vice. By various trials, made in this way, of ingots taken from the charge, some of which are broken when cold, hammered on the anvil while red, or cut, the knowledge of the point when no more oxide of copper remains, and the grain of the metal becomes sufficiently fine, is arrived at with considerable precision. Long and diligent observations are required to be able to detect this point with certainty, because the several assays vary to some extent in every variety of copper according to their malleability; and so with the repeated samples taken from any particular species from the first to the last during the refining. When the poling has not been continued long enough, the ingot, when cut and broken, appears almost devoid of metallic lustre, and has a brick red colour, and a fracture which is dull and granular. Upon continuing the action of the charcoal and the birch spars, each succeeding ingot shows an improvement in the grain, and also in the colour of the metal, in proportion as the required point is neared, till finally it assumes a beautiful silky lustre, and a fine pale red hue. When these characteristics appear, the refining is considered to be finished, and the assayer directs the workmen to withdraw the spar of wood, and prepare for casting. The fire which, from the commencement of the poling, was cut off from the metal by conducting the draught through another flue in the upper part is now redirected on it; and after the coating of scoria, which resulted from the ebullition of the metal and the combustion of the fuel, has been raked off, and a few shovelsful of charcoal thrown upon its surface, the superior flue is closed, and the heat carried through the furnace as usual. In this way the metal is retained fluid, and the layer of charcoal takes up any oxygen which may pass over it, so that there is no possibility of further oxidation. The men now proceed to cast the copper into moulds of suitable dimensions—such as are represented in Fig. 14—

Fig. 14.



using for the purpose ladles which have been coated with clay.

The utmost caution and expertness are required on the part of the refiner, in order to judge of the relative purity of each sample as he draws it out, and which varies with every variety of metal: for if the poling be prolonged only a few minutes beyond

the time at which the assay shows, from its silky grain and fine rose colour, that the refining is completed, it would deteriorate the product considerably. Under such a condition the grain becomes coarser, and the lustre, though still retained, loses the silky appearance of the well-refined metal. Should the poling be still further continued, it will render the grain of the metal rougher, the fracture fibrous and striated, and the brittleness will be increased even more than when it was in the *dry* state, in consequence of the formation of a carbide of copper. When such an occurrence happens the coating of charcoal is skimmed, and the bath exposed to the air passing in through the fire and rushing in at the doors, which has the effect of bringing it back to its ductile state once more. In like manner, if the metal is kept covered with charcoal during casting, injury will arise from the absorption of oxygen, and the refining will, in the language of the operator, go back. When this is the case, recourse must be again had to the spars of wood to reduce any oxide that may have formed.

Sometimes considerable difficulty is experienced in bringing the copper to that state of purity necessary to insure its sale; and when other metals are present, the gas liberated from the spars of wood fails to have a beneficial effect. In this case it is better to add some lead, and to rabble the bath thoroughly for some time: this metal, while divesting the copper of oxygen, forms a medium through which the iron, arsenic, tin, &c., are converted into oxides, and thrown off as scoria, on account of its great affinity for oxygen. Care must be taken, however, that the agitation is sufficient to bring every particle of the lead within the influence of the air at the surface of the molten mass, where it is converted into litharge and removed by the rake. Should any of it remain in the copper, it would occasion difficulty in lamination, by preventing the scales from falling cleanly off the surface. The results of the charge operated upon, and represented as follows:—

| | |
|---|---|
| Coarse copper, | 0·954 |
| Earthy matters, sand, | 0·013 |
| " " brick and clay, | 0·021 |
| Oxygen of the air, | 0·012 |
| | 1·000 |

are as follows:—

| | |
|---|---|
| Saleable copper, | 0·908 |
| Slag for operation four, | 0·055 |
| Furnace waste do. do. | 0·022 |
| Copper sweepings do. do. | 0·002 |
| Sulphurous acid, | 0·013 |
| | 1·000 |

Patented Improvements.—Although the result of all experiments has been to prove the above process (modified in details according to the character of the ore to be treated and the quality of metal desired) to be the best on the whole, yet it may be well to give an account of some of the various patents that have at different times been granted for improved methods, since, even when these have not been generally introduced, something is sure to be learnt from the experiments and attempts.

*Brankart's Patent* was especially intended for the reduction of rich South American and other foreign ores. The principle of the patent is the conversion of sulphide of copper into a sulphate, extracting this from the gangue with water, and precipitating the metal by iron, which is, during the operation, converted into sulphate or copperas. The ores suited to this treatment are copper pyrites and sulphides from the Cuban mines. These are known as *Cobre ores*, and generally contain from 15 to 25 per cent. of metal, together with iron and other impurities. The course which the patentee recommends is to reduce the substance to powder, and then expose it during several hours to the heat of a calcining furnace, by which considerable quantities of the sulphur are dissipated as sulphurous acid, whilst another portion is converted into sulphuric acid, which combines with the oxide of copper. When this process has been sufficiently prolonged, the ore is raked out and thrown at once into large vats filled with water. The sulphate of copper is dissolved, and after a short time the liquor is slowly allowed to flow out into another tank. The residue which remains on the bottom of the vat, and which still contains some metal, either as oxide or sulphide, is dried, and afterwards mixed with a proper quantity of the fresh ore and heated as before, when, by the reaction of the air the sulphides and sesquioxides of iron, the sulphur will be converted into sulphuric acid; this unites with the oxide of copper, and forms a sulphate which may be washed out in the manner already indicated. When the proportion of sesquioxide of iron increases in the exhausted ore no copper is lost, for it causes the formation of enough sulphuric acid from the sulphur in the crude mineral as will combine with the whole of the copper that may be present. Quantities of iron are thrown into the liquor, and the metal precipitates in the course of a few days, after which the supernatant liquor is decanted, the precipitate washed well with water, then dried and submitted to a slight process of refining. The sulphate of iron is obtained from the liquor by evaporation. (See Wet Processes.)

*Rivot and Phillip's Patent.*—This so far agrees in principle with Brankart's that it is founded on the greater affinity of iron than of copper for the impurities. But in this process it is the *oxygen* that is made to combine with the iron, oxygen which is left combined with the copper after the ore is roasted *dead*, that is, when all the sulphur has been expelled. Bars of iron are then introduced through apertures made for the purpose in the hearth. As soon as these come into contact with the heated material, which at this stage consists principally of oxides and silicious matters, reduction of the oxide of copper ensues owing to the greater affinity of the iron for oxygen, especially in the presence of sand. The oxide of iron which is thus formed is contained in the slag, which is subsequently skimmed from the metallic bath, united with silica. This operation is most suitable for rich ores; but if they contain other

metals which affect the quality of copper, they cannot undergo smelting in this way, as the arsenic, tin, &c., would remain in part with it, and render it unfit for general use. Were it not for this, and the destruction of a large quantity of iron, the process might be brought into requisition, as by it very fair metal could be obtained at one operation.

*Napier's Patent.*—In smelting, the chief object is the separation of the silicious earthy impurities, the iron, and the sulphur usually associated with the copper; the quicker and more completely this is performed, the more profitable will be the method of working, for not only will saving in labour and fuel be effected, but the quality of the metal will be improved. In the method under consideration, it is directed that the ores from Cornwall and such as are similar to them, as well as those imported, be calcined in an ordinary furnace. This product is next mixed with a quantity of rich Cobre ores, or other sulphides having a high percentage of metal, the proportion being inferred from their analysis, as well as from the fact that the iron and silica combine to form a clean fusible slag, and that the resulting matt should contain from 30 to 50 per cent. of copper. The mixture is now to be introduced into a reverberatory, and fused as when preparing *coarse metal* or *matt*, and when the fire has thoroughly effected the liquefaction of the constituents the scoria is raked. At this stage a quantity of soda ash (crude carbonate of soda) or salt cake (sulphate of soda) is introduced and rabbled with the mass. The alkaline salt undergoes decomposition and becomes a sulphide, which dissolves any arsenic, tin, or antimony that may be present, and carries them off in combination when the mass is afterwards treated with water. If salt cake be taken, it is necessary to mix it with charcoal to reduce the sulphuric acid more effectually, and bring it to the state of sulphide; the quantity used being 20 to 30 lbs. to 1½ cwt. of the soda salt, and this mixture serves for 1 ton of the matt. A very short time suffices for the decomposition of the sulphate, so as to cause it to react upon the impurities already noted. When this decomposition is considered to be finished, the furnace is tapped, and the mass cast into moulds of a rectangular or other suitable shape. As soon as these solidify, so as to bear removal, they are put into tanks filled with water, where they disintegrate into an impalpable powder. After some time the water is siphoned, or otherwise allowed to flow off, and the sediment washed to remove the soda compound, and with it the arsenic, tin, or antimony which it dissolved, if they were present.

The finely-divided residue is next dried, and submitted to heat in a calcining furnace till the last traces of sulphur are eliminated; this, owing to the minute state of division of the matt, is done in twenty-four or, at most, thirty hours. Having thus reduced all the copper to the state of oxide, the latter is now to be mixed with a quantity of fresh mineral which is free from sulphur and arsenic, but rich in silica, and with coal or charcoal, and the compound treated in a smelting furnace in the ordinary way; reduction will take place, and a slag will be formed which will not retain much either of the metal or of its oxide.

Birkmyre is another of those who have experimented on copper reduction. He burns the copper pyrites so as to recover all the sulphur in the state of oil of vitriol and sulphates of iron and soda. The mineral is finely ground, then placed upon trays, which are sufficiently capacious to hold about 1½ cwt., and these are introduced into kilns similar to those in common use for burning pyrites.

Before submitting the ore to the heat of the kilns, it is mixed with a quantity of nitrate of soda, in order that the sulphur may be converted into sulphuric acid during the combustion. After an hour's calcination the trays may be withdrawn and their contents cast into water, where the sulphates of copper and soda produced during the foregoing part of the operation are washed out, leaving the gangue in the bottom of the tank.

The copper in this, as in Napier's process, is entirely freed from arsenic, which is expelled in the form of arsenious acid during the roasting. The metal is recovered from the saline solution by precipitating it with iron.

Charles Low proposed to simplify the labour of smelting by employing a combination of binoxide of manganese, plumbago, nitrates of potash, soda, or lime, and charcoal, as a flux. The proportion in which these are blended with each other is as follows:—

| | | |
|---|---|---|
| 42 | parts | of binoxide of manganese. |
| 8 | " | plumbago. |
| 2 | " | nitrate of potassa, soda, or lime. |
| 14 | " | wood charcoal or anthracite. |

While the fusion for matt is going on, a quantity of this flux is added and mixed intimately by rabbling, in order to cause the separation of the silicious and metallic impurities as scoria, and also to render this more fluid than it is on ordinary occasions, that it may be less able to retain any of the matt or metal. Twenty-five pounds are first used; and when the fluid slag rises to the surface it is skimmed, and the above weight of the flux again rabbled with the molten mass, and the scoria which it produces separated as before, and so on till the workman judges that the metal has arrived at a sufficiently forward state for it to be run off.

*Truman and Cameron's Patent* recommends the following course:—When sulphide of copper, or substances containing sulphur, are to be operated upon, the patentees roast them in the ordinary way to procure a matt of coarse metal, which is afterwards ground, and a portion submitted to analysis, to ascertain whether tin, arsenic, or antimony is present. If these be detected, the powdered matt is boiled with a solution of caustic potassa for six hours, keeping the contents of the vessel well stirred during that time. The object of this is to remove those metals in the form of salts, namely, as potassium, stannate, arsenite, and antimonite. After the solution is drawn off, the residuary matter is calcined to remove all, or as much as possible, of the sulphur.

and produce an oxide, which is subsequently mixed with sulphide of copper in such a proportion that the oxygen in the oxide will be sufficient to form sulphurous acid with the sulphur in the crude ore. It is likewise necessary that the silica in the mixture should correspond with the iron, so as to yield a fusible slag; if, however, there is not enough silica present to take up all the iron, then a certain weight of sand, or preferably, the bottoms of old furnaces, called *cobbing*, must be mixed with it. The components of a charge which affords the metal with facility are thus stated, namely:—

| | | |
|---|---|---|
| 25 parts of calcined powder, having 47 per cent. of oxide of copper. | | |
| 12 parts of Cobre ores, containing centesimally, | copper, | 26 |
| | iron, | 26 |
| | silica, | 16 |
| | sulphur, | 32 |
| 12 parts of cobbing, | silica, | 72 |
| | copper, | 12 |
| | iron. | 6 |

About 2½ tons of this mixture are submitted to the furnace and fused; five hours after the charging the whole is rabbled, then allowed to rest, and the slags skimmed as they rise to the surface; the fluid matt is not drawn off as usual, but another charge is introduced and worked like the preceding, after which the furnace is tapped. A rich compound of copper and sulphur, free from iron or nearly so, is separated, and when calcined and fused in furnace it yields metal of good quality.

Foreign Modes of Copper-smelting.—The modes of smelting copper pyrites, and other sulphurous ores of copper described above, are those adopted in England and Wales. On the Continent, however, the minerals differ from those found in Great Britain, and a different mode of smelting is adopted.

Many ores are found besides the sulphides of copper; such are the oxides and suboxide known as *black* and *red* ore and the *azure* ore or carbonate. These require a special mode of working distinct from the routine described, while, as will be seen below, the quite other circumstances of the *Mansfeld* ore necessitates yet other treatment. A description of two or three of these continental methods will now be given.

*Copper-smelting at Chessy, in France.*—The ores of Chessy, near Lyons, in France, are the azure and red variety, the former not discovered there till 1812, and the latter in 1825.

The annexed analyses of the rich and poor class of *red* ore of this locality shows that their smelting is not a very difficult procedure:—

| | Centesimally represented. | | |
|---|---|---|---|
| | Rich. | | Poor |
| Suboxide of copper, | 86 | .. | 45 |
| Sesquioxide of iron, | 4 | .. | 20 |
| Aluminous and silicious matters, | 5 | .. | 30 |
| Water, | 4 | .. | 5 |
| Loss, | 1 | .. | 0 |
| | 100 | | 100 |

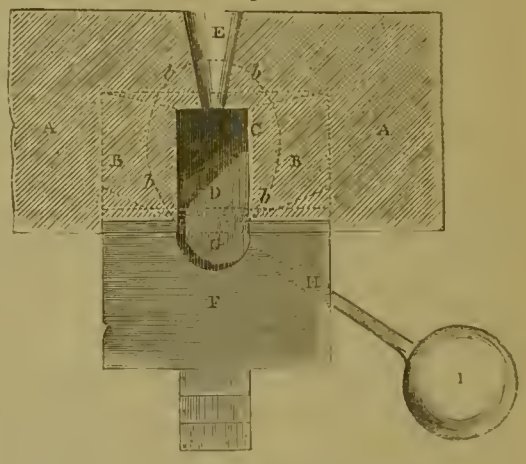
The composition of the *blue* ores likewise shows that they are capable of yielding a good return, and can be worked with comparative facility:—

| | Centesimally represented. | | | |
|---|---|---|---|---|
| | Rich ore after picking and washing. | Rich ore after sifting. | Poor ore after washing. | Poor ore after sifting. |
| Protoxide of copper, | 45 .. | 42 .. | 30 .. | 25 |
| Oxide of iron, | 1 .. | 4 .. | 2 .. | 5 |
| Aluminous and silicious matters, | 30 .. | 30 .. | 52 .. | 55 |
| Carbonic acid and water, | 23 .. | 22 .. | 15 .. | 14 |
| Loss, | 1 .. | 2 .. | 1 .. | 1 |
| | 100 | 100 | 100 | 100 |

These minerals are smelted at once in a furnace, called by the French *fourneau à manche*, shown in the annexed Figs. 15 and 16.

The first of these is a horizontal section on a level with the tuyere, or pipe which directs the blast, and the second an elevation. The base of the furnace, A A, is constructed of solid masonry, strengthened by transverse bars of iron. B B is a coating of refractory material, which is renewed every season; it is cemented to the masonry in the form of an ellipse, as shown in the dotted line. The two

Fig. 15.

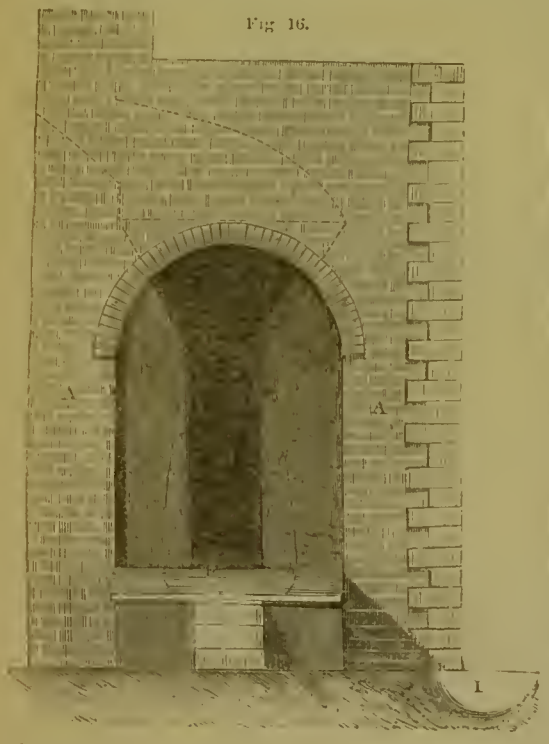



lateral faces are formed of gneiss, and the front one, called *fierrende*, is constructed of rectangular iron plates, coated with fire-clay; these are supposed to be taken off in the figure. C C shows the form of the coating at the time of the firing; it is a rectangular parallelopiped of about 6 feet in length, 5¼ in breadth, and about 3¼ feet in depth. D is the sole, composed of firebrick made from Bourgogne clay and pulverized quartz. E is the tuyere; its orifice is 3 inches in diameter. F is the platform or table, constructed of clay firmly beaten between the fore part of the furnace and three small walls which are bound by iron bars. Three steps are made in front for the convenience of the ascent of the workmen. G is a basin or crucible dug in the table in the front of the fire; it is made on a level with the sole of the furnace. It is coated with a mixture of clay and powdered charcoal, which preserves it from injury for weeks together. H is an inclined canal opening into the recipient, I, where the fluid collects.

The ore to be smelted in this furnace is mixed so that the mean content of metal will be about 27 per cent.; to this 5 per cent. of caustic lime are added,

together with a small amount of scoria. 200 lbs. of this mixture, mingled with about 250 lbs. of coke, are introduced into the furnace hourly when the latter is in good working order. As the fusion and reduction proceed, the melted metal and scoria flow out into the bath opposite the fire, from which the latter may be separated by skimming it off. In about twelve hours the basin opposite the fire is filled with metal, which may be run off in the ordinary way into the recipient, 1. Any scoria which may be carried over floats on the surface, and can be easily removed. A little water is next sprinkled upon the metal; its evaporation causes the formation of a solid crust, which is taken out of the bath by a circular implement. By continuing this operation the whole contents may be converted into cakes or discs of three quarters to one inch in thickness. The running takes place twice each day, and on the

Fig. 16.




whole there is about 13¾ cwts. of metal. It is necessary to repair the basin opposite the fire once a week. The products of the foregoing fusion are the ordinary slags formed in the furnace and those produced in the recipient, the black copper and other matter being carried off in the flue. The scoria is of three kinds, the blue, the black, and the red, but some of these retain only very small quantities of copper, as seen in the annexed table:—

| | Blue Scoria. Per cent. | Black Scoria. Per cent. | Red Scoria Per cent. |
|---|---|---|---|
| Silica, | 55·0 | 56·0 | 58·6 |
| Alumina, | 7·0 | 9·0 | 5·0 |
| Lime, | 24·6 | 27·0 | 16·0 |
| Protoxide of iron, | 11·9 | 7·0 | 12·6 |
| Protoxide of copper, | 0·5 | 0·7 | 0·0 |
| Suboxide of copper, | 0·0 | 0·0 | 6·6 |
| Loss, | 1·0 | 0·3 | 1·2 |
| | 100·0 | 100·0 | 100·0 |

The blue slags contain very little oxide of copper; they are formed when lime is present in sufficient quantity. Black slags are produced when the above earth is wanting, and the iron of the ore vitrifies the silicic acid of the mixture; they have more copper than the blue variety, and are often coated with a red scoria, which is indicative of the combination of oxide of copper with silica. Red scoria is composed of silicate of iron and copper, and is evidently the result of not having the sand, quartz, &c., proportioned to such bases as would take it up and wholly prevent its union with the copper; this, however, is not the only cause, for the same result follows the application of a high temperature in the furnace. The formation of these slags rich in copper is a sure sign that the heat of the furnace is too elevated, which causes them to run so quickly that the copper cannot be sufficiently reduced.

It may be conceived, likewise, upon similar grounds, that minerals which are very rich are more difficultly treated than when they afford a large amount of slag; because the time necessary to effect the fusion in the latter instance is sufficient to reduce the metal completely, and hence, when the fused mass runs out into the crucible, scarcely any red slag is found in it. A proper amount of fluxing material always keeps the scoria free from copper, and any derangement in the working may be readily rectified by altering the mixtures operated upon, or diminishing the blast.

The composition of the scoria thrown off from the metal, after it flows over to the recipient, is—

| | Centesimally. |
|---|---|
| Silica, | 30·5 |
| Protoxide of iron, | 55·5 |
| Sulphur, | 2·3 |
| Iron, | 1·8 |
| Copper, | 4·4 |
| Sand, | 0·5 |
| Loss, | 5·0 |
| | 100 0 |

This slag differs from the foregoing in not containing lime. The action of the air upon the bath of metal oxidizes a large quantity of the iron as well as some copper, and these reacting upon the silicious coating of the crucible, occasion its formation.

The black copper which results from these operations is of very variable composition. When the scoria is black the metal is found charged with iron to the extent of 7 or 8 per cent. Even in the same running much difference may be observed in this respect, for the copper being denser than the metals accompanying it, settles to the bottom in large quantities, and hence the last cakes are richer than the first. The annexed is the mean of several analyses by M. Margerin of black copper thus obtained:—

| | Per cent. |
|---|---|
| Copper, | 89·30 |
| Iron, | 6·50 |
| Protoxide of iron, | 2·40 |
| Silica, | 1 30 |
| Sulphur, | 0·34 |
| Loss, | 0·16 |
| | 100·00 |

The above kinds of ore might be worked with advantage in a reverberatory furnace heated with coal, mixing therewith some powdered charcoal, sufficient lime, and a little scoria to facilitate the fusion. The copper would thus be obtained entirely or nearly free from iron and sulphur.

For many years past an ore called *black mine* has also been obtained from Chessy, which is composed, according to THIBAUD and BERTHIER, of—

| | Per cent. Rich mineral. | | Per cent. Another sample. |
|---|---|---|---|
| Protoxide of copper, | 12·00 | 14·0 | 22·67 |
| Copper pyrites, | 56·35 | 46·1 | 20·15 |
| Iron pyrites, | 25·01 | 36·3 | 8·94 |
| Sulphate of barium, | 2·60 | 0·0 | 28·80 |
| Sesquioxide of iron, | 0·00 | 3·0 | 9·22 |
| Loss, | 4·04 | 0·6 | Sand, &c., 20·22 |
| | 100·00 | 100·0 | 100·00 |

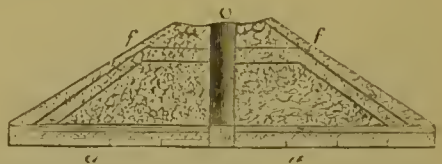
It is smelted in a furnace similar to that last described, without any previous preparation, except that half of the scoria from a foregoing charge, together with half from the smelting of carbonated ores, which are rich in lime and alumina, is added, to render it more fusible. In this way a matt is obtained which is afterwards submitted to five or six calcinations, in the same manner as that followed at Swansea and other places; and the decomposition of the sulphur compounds by the oxides is effected here in the way already explained. The sulphate of barium is decomposed by the coal used into sulphide of barium, which, reacting upon the oxide of iron, gives rise to sulphide of iron and baryta, which combines with the silica, and passes off in the scoria. An excess of heavy spar, however, is not desirable, as it occasions the presence of too large a quantity of sulphide of iron in the matt, which must be expelled afterwards at the cost of time and labour.

*Copper-smelting at Mansfeld in Germany.*—At Mansfeld in Prussia there is a cupreous schist, or rather shale, which, though yielding but a small percentage of the metal, is successfully smelted. This *kupferschiefer*, as it is called, which belongs to the Permian formation, is a bed of somewhat bituminous shale, a foot or two thick, of which, however, only a portion a few inches thick has enough of copper to justify its metallurgical treatment. This portion contains about 2½ per cent. of copper in the form of various sulphides, as well as other copper minerals. Of silver, also, there is a noteworthy amount, and there are small quantities of other metals.

The *first operation* is the roasting of the ore in mounds; in this the burning, which is begun by lighting some piles of brushwood laid beneath, is continued by the combustion both of the bituminous matter and the sulphur contained in the schist; not all the sulphur, however, should be eliminated. The mounds continue burning, according to the state of the weather and the size of each, for from two to four months. During the operation the ore loses about one-tenth of its weight, becomes friable, and acquires a yellowish-grey colour.

On the Lower Hartz, where there is an iron pyrites containing about 5½ per cent. of metallic copper, together with more or less antimony and arsenic, the method of procedure is such that some of the sulphur is recovered during the preliminary calcination to which the ore is submitted. The manner in which this is performed is shown in Fig. 17, which represents a vertical section of a mound in the state of calcination. The form is that of a truncated quadrangular pyramid, the base of which is composed of

Fig. 17.




wooden billets, *a a*, laid in such a way as to allow an access to the central wooden chimney, c. At the base of the latter some charcoal is kindled, and the heat penetrating the pyritous mass, *d d*, suffices to effect a decomposition by which a portion of the sulphur is expelled as sulphurous acid, and another quantity as free sulphur, which is condensed in the upper part of the mound. It requires careful attention for two or three days, in order that the fire may take hold; when this is done the mound is coated exteriorly with matt and refuse mineral, as shown at *f f*, so as to direct the draught to the top. By the combustion of the wood on which the mineral rests the latter is ignited, and the heat developed by the conversion of one portion of the sulphur into sulphuric acid is sufficient to maintain the whole in a

Fig. 18.

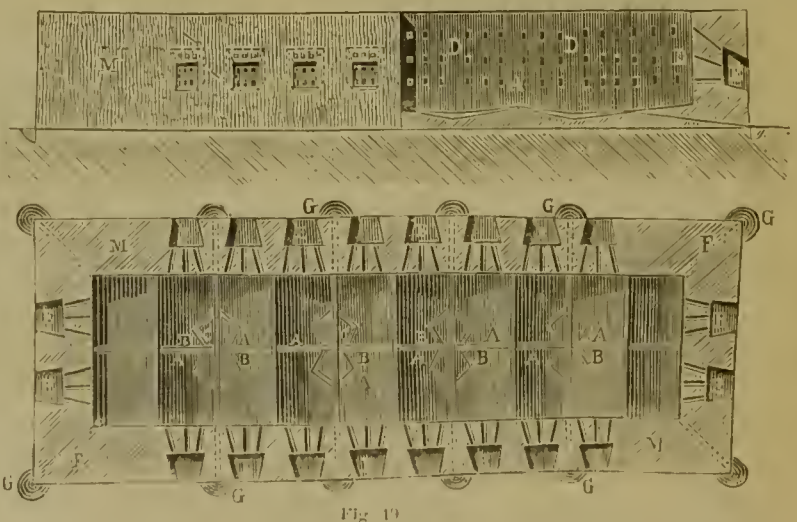
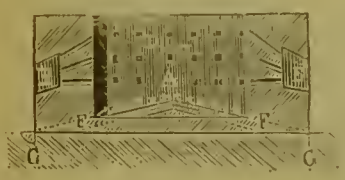



Fig. 19

state of ignition. A number of cavities are made in the top of the mound, into which, as the upper portion becomes surcharged with sulphur, it collects in a fluid state, and is thence removed by an iron ladle, and cast into water to be further purified. After the first calcination the mound is turned over, and such parts as had agglomerated are subjected to a repetition of the preceding process.

At Agordo the roasting is effected by the kiln shown in the accompanying figures. Fig. 18 depicts the kiln partly in elevation, partly in section. Fig. 19 is a horizontal section along the line of the doors. Fig. 20 is a vertical section across the furnace. Thick walls, M, surround the chamber, A, which is divided into sections. The bed of each section is a low pyramid, A A, having its apex at the centre of the furnace. Channels, B, are cut along the lines of junction of the bed plates, and also on the faces of the pyramid at C. Nine other channels communicate through the walls, M, with each of the chambers, which serve to collect the sulphur. The canals, F, conduct the liquid sulphur into the globular receptacles, G. The kiln is charged by building chimneys of lumps of ore upon the top of the pyramids, and after covering the gutters with flat stones, filling in the whole space between the chimneys and the walls with alternate layers of coarse and fine ore, with occasional layers of wood, to facilitate ignition. The roasting is complete in from five to six months.

Fig. 20.




The calcining completed, the Mansfeld mineral, in readiness for the *second operation*, is mixed with such ingredients as will promote its fusion. This mixture consists of relative weights of the schist, according to its composition, which is very variable, fluor spar, scoria rich in copper, and other refuse. Thus—

| | | |
|---|---|---|
| 20 | cwts. | of ferruginous slate, |
| 14 | " | calcareous slate, |
| 6 | " | argillaceous slate, |
| 3 | " | fluor spar, |
| 3 | " | rich slags, |

constitute an ordinary charge for the blast furnace in which the operation is performed.

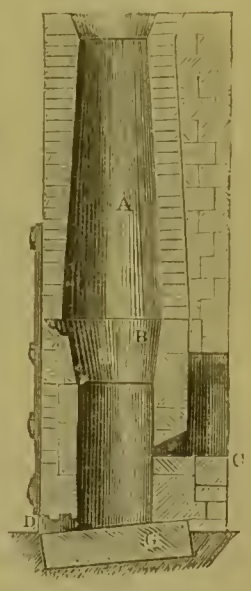
Fig. 21 represents an elevation, Fig. 22 a vertical section, and Fig. 23 the base of the furnace used on this occasion; the last showing the outlets into the crucibles which receive the matt which results. In these figures A represents the shaft, B the rest, C the tuyere, D the apertures through which the fluid flows by the channels, E E, into the basins, F F—Fig. 23. The shaft is constructed of firebrick, lined at the back with some refractory and non-conducting material, generally rubbish stones, and the parts adjoining the *tuyeres* of pudding-stone, through which the heat passes very slowly. The hearth-stone, G, is inclined to the openings, D, to facilitate the effusion of the matt into the basins. Generally, the height of this furnace is from 15 to 18 feet; the breadth at the tuyeres, which are 2 feet from the sole, about 26 inches, and at the widest part 3½ feet; the whole is surmounted by a chimney of 40 or 50 feet high, which conducts the gases out of the reach of the workmen.

The charge above described is introduced in portions alternating with the fuel, which is coke, and by the aid of the blast is melted in about fifteen hours. During the melting, the outlets, D, are opened

Fig. 21.



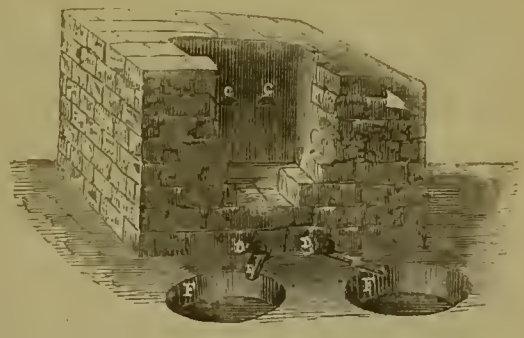

Fig. 22.




alternately as each basin is filled with the molten mass, which flows out to one or the other continuously. From these receptacles the matt is removed in the form of circular plates, which are lifted off when sufficiently cool from the surface of the still liquid sulphides remaining in the bottom of the cavity.

The yield is about one-tenth of the weight in a regulus, which is called *rohstein*, containing from 30

Fig. 23.




to 40 per cent. of copper, the remainder being a slag called *rohschlacke*. This *rohstein* corresponds to the *coarse metal* of the English process. New furnaces of greater size have latterly been erected; these have six tuyeres for a blast heated to 280° C., and they are made so that the waste gases are collected and utilized; otherwise the process with them is the same as in the older sort of furnace.

The *third operation* is the roasting of the *coarse metal*; this is done either in kilns or stalls, of which three sides are of strongly-built walls, the fourth of movable stones; some brushwood is required to start the combustion, and then the sulphur itself of the regulus burns. One roasting (though lasting ten or twelve days) is not enough for all the material; some of it has to undergo the same thing two or three times.

In the *fourth operation* the product of the last is fused with the addition of the richest slag from the previous melting, as a flux. Formerly the furnace employed for this was a cupola, but now a reverberatory furnace, on the plan of the melting furnaces of the English method, is used. The result is a regulus containing over 60 per cent. of copper and a proportion of silver. It goes by the name of *spurstein*, and may be called by us *fine metal*.

For some of the remaining processes of the system as at present carried out we follow J. A. Phillips. The *fifth process* is a grinding of the *spurstein*, which had previously been granulated; it is here ground fine in a mill and sifted.

The *sixth process* is an almost complete roasting: it is effected in a reverberatory furnace, the result being the conversion of the copper sulphide into oxide, and of the silver (which has before been mentioned as occurring in the ore) to the state of sulphate.

The *seventh process* has for its object the separation of the silver; it is a lixiviation of the last roasted product. The sulphate of silver is dissolved, the solution being run into other vessels; then from this solution silver is obtained by means of metallic copper, which precipitates it.

The *eighth process* is a melting of the residue of the lixiviation; it is done in a blast furnace similar to that used for the second operation; the oxidised product is mixed with flux and with coke for its reduction. The reduced metal (called *black copper*) contains 98·8 per cent. of copper; there also results a proportion of regulus of sulphide of copper, which is treated over again, and a slag, most of which is thrown away.

The *ninth operation*, and the last, is the refining of the black copper. It is done in two different ways. Figs. 24 and 25 exhibit the kind of hearth employed in one of these two. *a* is a hemispherical crucible 16 inches in diameter, and rendered fireproof by a luting composed of two parts of powdered charcoal and one of fireclay; *c* is an iron curb for keeping the fuel from being scattered about during the melting; *b* is the masonry, and *t* the tuyere of the hearth. The mode of charging is to fill the crucible with charcoal in an ignited state to desiccate it, if required. When this is done, more fuel is introduced, together with pieces of black copper, which are deposited opposite the tuyere. The blast is admitted by degrees, and as soon as the metal of the first charge has been fused, a further quantity is put in, with as much charcoal as will effect the reduction, and the work is continued till the crucible becomes nearly full of metal. The scoria, as it is produced, flows off through an opening, *d*—Fig. 25—into the receiver, leaving the metal at the bottom. After the whole of the black copper requisite to form a charge has been operated upon, the attendant begins to examine the product in the usual way, by taking samples out of the bath with an iron rod, and immersing them in cold water. When the assay appears brownish-red on the outside, and of a coppery lustre interiorly, together with exhibiting much brittleness, the refining is said to be finished. The blast is now cut off, and the cinders and slag skimmed with the rake; some cold water is next sprinkled upon the surface of the mass, and as soon as a solid crust is formed, it is removed and cast into cold water to prevent oxidation; more water is again thrown upon the metal, when another cake is formed, which is deposited in the tank in a similar way, and so on till the whole is converted into rosettes. 2¼ to 2½ cwts. form the charge for the furnace of the ordinary size; but sometimes as much as 7 cwts. may be operated upon in one of these hearths. For the first, three quarters of an hour are occupied in the refining, and about 1½ cwt. of metal in rosettes are obtained; but in the larger kinds of furnaces two hours are required. This product usually contains from 1 to 2 per cent. of other metals, such as lead, silver, iron, and aluminium. The first slag which is thrown off in this process has a greenish colour, and retains a large quantity of oxide of iron, but little copper; the next scoria, however, has a deep red appearance, and retains a considerable amount of suboxide of the metal, and, therefore, is subjected to further operations in the preparation of the black copper. *Rosettes*, as thus prepared, are never sufficiently refined to allow the copper to be rolled out into sheets, or manufactured into the ordinary articles; consequently it has to undergo a further treatment. The plates are melted in the hearth above described, the surface of the bath being covered with charcoal, in order to deprive the metal of oxygen. Samples are taken from time to time, and examined with great precision, and as soon as the true grain is attained the metal is cast into ingots. Sometimes the action of the charcoal is prolonged beyond due limits, and in such cases the product becomes injured: to bring it back, the refiner strips it of the charcoal, and directs the blast upon it, in order to expel any carbon which might have been taken up. By operating in this way, and with great caution, the bath is

Fig. 24.

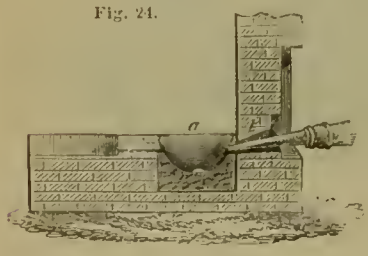
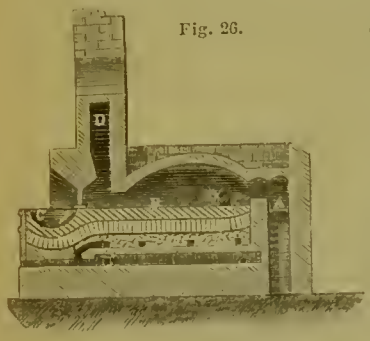



Fig. 25.



ultimately brought to its greatest degree of malleability. This metal bears a very high character for its purity, but it is said that it never excels the *selected refined* of the English smelter.

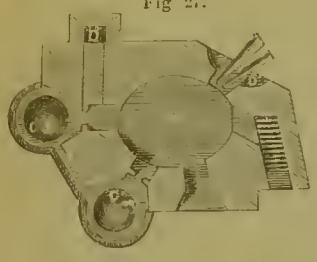
Fig. 26.



The other form of the process is a remelting of the black copper in a reverberatory furnace; this, again, may be of two kinds. Figs. 26 and 27 illustrate one in which a blast is used as well to facilitate the refining, where o is the tuyere, B the elliptical bed, C C two receivers, and D the chimney.

About 3 tons of black copper make a charge; being melted, the impurities become oxidized and form a slag, which is raked away; when it is judged that this operation has gone far enough, the metal is led into the receivers, whence it is taken in the form of rosettes in the way described above. The other kind of reverberatory furnace used is similar to that in which refining is done during the English process; the operation, indeed, is here identical with that just named—first an oxidation is effected, and then poling is resorted to.

Fig 27.



The other form of the process is a remelting of the black copper in a reverberatory furnace and poling, as in the sixth process of the English system. From this melting the copper is cast into various shapes to suit the wants of purchasers and manufacturers, and then may succeed the other processes of manufacture, as of rolling for the production of copper sheets.

*An Older Form of the Mansfeld Process.*—This, which now, we believe, is disused, is a different treatment of the *spurstein*, and itself results in *black copper;* it may therefore be said to stand for the fifth, sixth, seventh, and eighth operations described above.

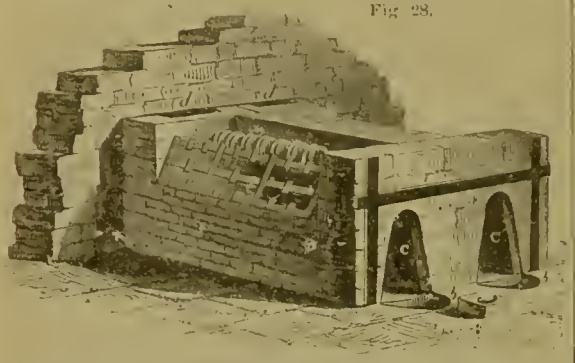
First, the *spurstein* is roasted, not in a furnace but in kilns, as many as six consecutive times during a period of seven or eight weeks. Brushwood and charcoal being interlaid with it, air is conveyed to the lower part of the mass, to maintain the combustion, by channels made in the walls of the compartments where the process is carried on; these open inwardly at the bottom. The front wall of the kiln is composed of stone, built loosely, and with the view of keeping the charge in one compartment from intermixing with that in the opposite. When the matt has been calcined in the first of these apartments, it is transferred to the next, and there again interstratified with wood and charcoal as before; when the roasting is effected here, it is thrown into the third, and so on in rotation till it comes to the sixth, where the calcination is finished. The resulting product is called *gahrrost* by the Germans; it resembles in colour red copper ore, but sometimes it has a bluish-grey shade; it is brittle, and contains some of the copper reduced, and also more or less sulphate of copper, arising from the oxidation of the sulphur by the oxides. It is necessary to remove this by lixiviation, an operation which is carried on in a series of vats fixed in an incline, so that the liquor in the upper one flows into each in succession till it comes to the lowermost, and during its passage takes up as much of the salt as will make the solution so concentrated as to require very little evaporation to crystallize it. This washing is sometimes carried on after each roasting, and the sulphate of copper formed in each compartment extracted. Finally, the calcined matt is melted in the cupola furnace with about a quarter of its weight of the lixiviated matt from the first fusion, when this is of a good quality, one-sixth to one-tenth of its weight of rich copper slags, and a due admixture of charcoal or coke; the charge varies from 3 to 4 tons, and the period of smelting extends over twenty-four hours. This operation yields black copper, and a slag of various degrees of richness; but the former, being the heavier, sinks to the bottom of the crucible, from which it is removed in discs, as already described. The slag is subsequently roasted with other matt, and then smelted to divest it of the metal.

This black copper is, however, not that product of the same name, free from silver, which results from the eighth operation of the system as now carried on. The means by which the separation of the silver was done in this older system is one of extreme ingenuity and interest; one that deserves description, even though not at present practised. The principle of operation is that when copper is alloyed with lead, and afterwards heated to a certain point, the lead will separate and carry with it the silver, flowing away from the copper, which is left as a spongy mass; such a process is called *eliquation.* In practice it is done by fusing 3 parts of black copper and 10 or 12 parts of lead, or an equivalent proportion of litharge rich in silver, in a cupola furnace, and running the molten mass out into moulds, where it is rapidly cooled by means of water, and removed in the shape of discs of about an inch or less in thickness. These are then to be heated on a smelting hearth similar to that represented in Figs. 28 and 29 to the necessary degree, which determines the separation of the argentiferous lead by melting or sweating; this temperature is kept up as long as required. When as much as possible of the lead is removed the discs appear in their original form, but very porous, still retaining an appreciable amount of the alloyed metals.

The hearth is composed of two cast-iron plates resting upon ledges of brickwork, and inclined towards each other, leaving a space, S, under which

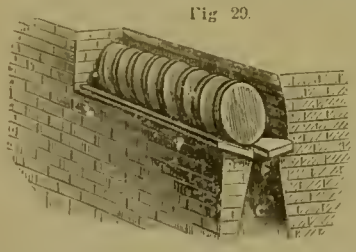
is a hollow channel, c. The discs of alloyed metal are placed perpendicularly upon these plates, their contact being prevented by pieces of wood. Charcoal is then thrown around and between them, the dividers being withdrawn; this is afterwards ignited by introducing some lighted faggots into the channel, c, and the smoke and gases carried on

Fig. 28.



through draught-holes or chimneys, *d d*, in the walls of the hearth. As the plates become heated, the lead begins to flow, and falls upon the floor of the channel, which, being inclined, conducts it to a receptacle, *b*, whence it is taken and cast into moulds. Heat is applied to the plates as long as any metal separates, and when no more exudes they are taken to another furnace in which the temperature is more elevated, and where any portions still retained are recovered, and the black copper is left purer than after the first heating. It still retains some lead, together with traces of silver, but the former is entirely dissipated in the refining to which the cakes are subjected.

Fig. 29.



Wet Processes.—These have of late years become increasingly important. On the one hand, large quantities of copper are now extracted by them from a product which till recently was not applied to the production of that metal, namely, burnt pyrites; and on the other poor ores have, with more or less of success, been subjected to such processes with the thought that copper can be more economically treated in the wet way than by the smelting processes hitherto described, so that poor ores might be utilized which otherwise would be counted quite unprofitable.

The wet process may be applied to ores which contain small quantities both of tin and copper, as well as an amount, large or small, of arsenic. In such cases all three products are obtained.

The ores are first calcined by one of the methods that have in detail been described in the article Arsenic. The calcined ore is then thrown into *laching* tanks, containing a strong solution of common salt; these tanks are square, and have a false bottom of perforated boards, over which is a layer of canvas for filtering; in the tank the brine is heated by means of steam, and then is drawn off to the *precipitating* tanks. By these means the copper is converted into a soluble form (chloride), and is taken up by the liquor; while, in the precipitating tanks, it is again brought down by scrap iron placed in them, which decomposes the salt of copper, and causes that metal to be deposited. The precipitated copper is removed by shaking and washing once a month, while the brine is run off to be again used with the addition of some fresh salt.

In this way ores that have but 2 per cent. of copper can be profitably treated. The amount of salt (old and fresh together) that is used is 2 cwts. to the ton of ore; but if there be over 3 per cent. of copper, then 2½ per cent. of salt is required.

By a late development of this system, the *nascent copper process*, any silver that may be contained in the ore, having been dissolved with the copper in the form of chloride (a compound that the brine will dissolve), is precipitated in the lower tanks by the copper *at the moment when the copper is released by the iron.* The precipitate then contains both the copper and the silver, which latter is separated by a distinct treatment, generally in another establishment. One example of precipitate gave 59½ per cent. of copper with 139 ozs. of silver to the ton, the rest being mostly iron.

If the ore contain tin, then the residue in the laching tanks is treated in the ordinary way for that metal.

Various processes have at different times been in use for the treatment of copper ores by *hydrochloric acid;* these, though to some extent successful, have not been completely so or permanently profitable.

*Application of the Wet Process to Burnt Pyrites.*—This process now constitutes one of the most important branches of manufacturing chemistry in this country, inasmuch as nearly the whole of the sulphuric acid made is produced from cupreous pyrites, the cinders from the pyrites kilns being subsequently sent to the copper extraction works. As appears by the "Mining Records" for 1873, 324,000 tons of *burnt coppery pyrites* were thus treated in that year; and this quantity is increasing steadily, more particularly since the Rio Tinto mines in Spain have been reopened on a very large scale, and their lessees are pushing the ore into the market, thus stimulating the manufacture both of sulphuric acid and of copper from the cinders. It may be considered as an established fact now, that for ores containing no more than 4 per cent. of copper the dry smelting process is not economical, and the wet extraction process is the only one practically used for it; but this result is certainly owing, to a great extent, to the possibility of recovering the iron as well as the copper by means of the wet process. Copper extraction by the wet process has thus become an appendage to sulphuric acid making, and it is naturally carried on extensively near the centres of that industry, that is, on the banks of the Tyne,

in South Lancashire, near Glasgow, and near Birmingham. The process now carried out in all these localities is as follows:—

The three largest mines from which cupreous pyrites is exported to this country are those of San Domingos in Portugal, of Tharsis and of Rio Tinto in Spain. They all contain from 47 to 49 per cent. of sulphur, and, on an average—

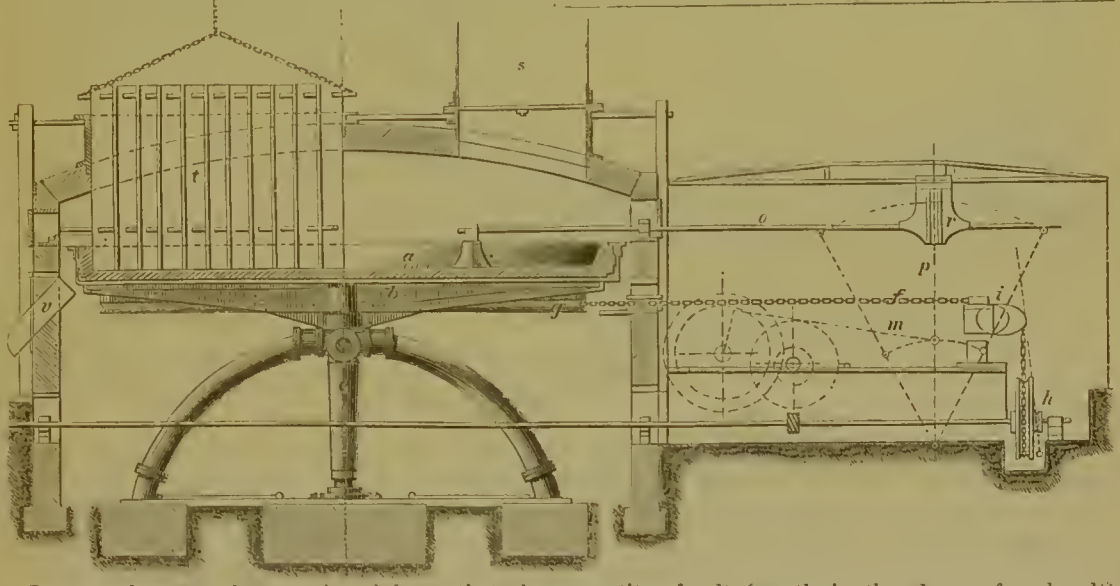
| | Copper. Per cent. | | Silver. Ounces per ton. |
|---|---|---|---|
| Rio Tinto, | 3·80 | .... | 1·20 |
| Tharsis, | 3·50 | .... | 0·75 |
| San Domingos, | 3·70 | .... | 0·75 |

There are several smaller mines in Spain and in Norway from which pyrites is also sent to this country.

As stated above, these ores are first used in the manufacture of sulphuric acid, both in alkali and manure works, the results being that the metallic sulphides are mostly converted into oxides. The following are analyses (according to Mr. Gibb) of the burnt ore from different sources:—

| | Rio Tinto. | Tharsis. | San Domingos. | Ytteroen. |
|---|---|---|---|---|
| Copper, (calculated as $Cu_2Fe_2S_3$,) | 1·65 | 1·50 | 1·55 | 1·01 |
| Iron, (calculated as $Cu_2Fe_2S_3$,) | 3·64 | 3·23 | 3·76 | 3·33 |
| Sulphur, (calculated as $Cu_2Fe_2S_3$,) | 3·53 | 3·15 | 3·62 | 3·10 |
| Cupric oxide, | 2·75 | 2·56 | 2·70 | 0·39 |
| Zincic oxide, | 2·02 | 0·55 | 0·17 | 6·46 |
| Plumbic oxide, | 0·47 | 0·70 | 0·84 | 0·06 |
| Silver, | 0·0037 | 0·0023 | 0·0023 | — |
| Cobaltic oxide, | 0·007 | 0·032 | 0·033 | — |
| Bismuthic oxide, | 0·013 | 0·010 | 0·013 | — |
| Calcic oxide, | 0·20 | 0·25 | 0·28 | 2·30 |
| Ferric oxide, | 77·40 | 77·00 | 78·15 | 68·06 |
| Sulphuric anhydride | 6·10 | 5·25 | 5·80 | 6·56 |
| Arsenic anhydride, | 0·24 | 0·17 | 0 25 | 0·05 |
| Insoluble, | 1·45 | 5·85 | 1·85 | 8·74 |
| | 99·47 | 100·26 | 99·32 | 100·06 |

Fig. 30.




It must, however, be mentioned here, that the percentage of sulphur in burnt ores varies extremely, even in the same works, and to a very much larger extent from different works. Some are said to burn it down to 2 per cent., whilst others leave as much as 8 or 10 per cent. in the "cinders." The latter is excessively bad work, but from 4 to 5 per cent. sulphur is not considered excessive, and about as much or even more sulphur is really necessary for carrying out the wet copper extracting process. If the pyrites has been burnt too well, the copper extracting works have to add a little unburnt pyrites to the cinders, in order to have a sufficient quantity of sulphur present for the first stage of their process. It consists in calcining the burnt ore with sodium chloride (common salt) up to a certain point, viz., so far that the copper is nearly all converted into chloride, whilst as little as possible of the iron is converted into chloride, which would of course be soluble. The burnt ore is first of all crushed to a fine powder between fluted rolls, and the necessary quantity of salt (mostly in the shape of rock-salt) is added during the grinding. It amounts to from 10 to 20 parts for 100 cinders, for the ordinary furnaces worked by hand, but only to 7½ parts of salt for 100 cinders when intended for Gibb and Gelstharpe's revolving cylinder. The mixture is sieved through a cylinder sieve covered with wire gauze of eight holes to the lineal inch, and run in iron wagons over the calcining furnaces, into which it is charged as required.

There is a great variety of calcining furnaces in existence, which can be classed under the following heads:—

1. *Reverberatory Furnaces of the Ordinary Kind.*—These were used at first, but have gone almost entirely out of use now.

2. *Mechanical Furnaces* (patented by Gibb & Gelstharpe in 1872).—In these the hearth is formed of a circular cast-iron horizontal pan, kept constantly revolving, whilst the ore is turned over and exposed to the oxidizing flame of the furnace by a

plough reciprocating slowly in a radial line of the circle of the bottom. The revolution of the pan and motion of the plough are both attained by simple gearing from one shaft. Arrangements are

Fig. 31

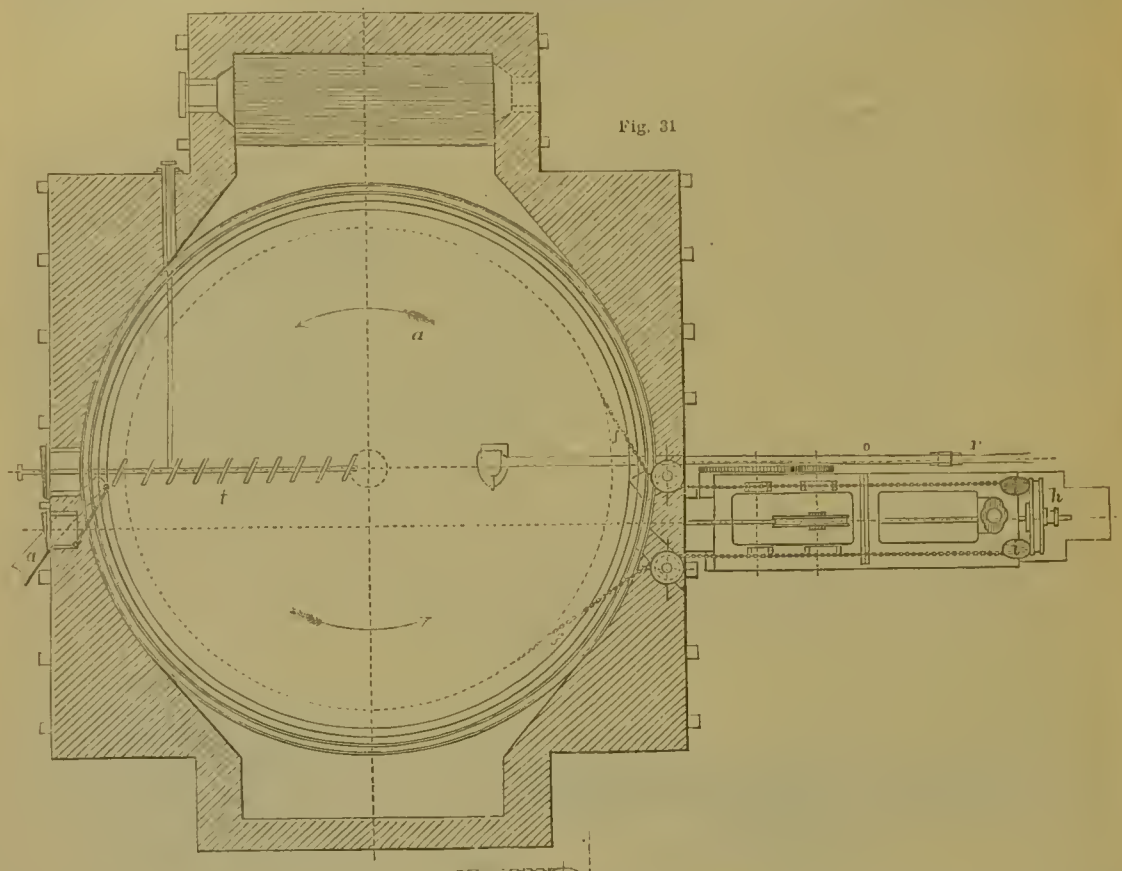
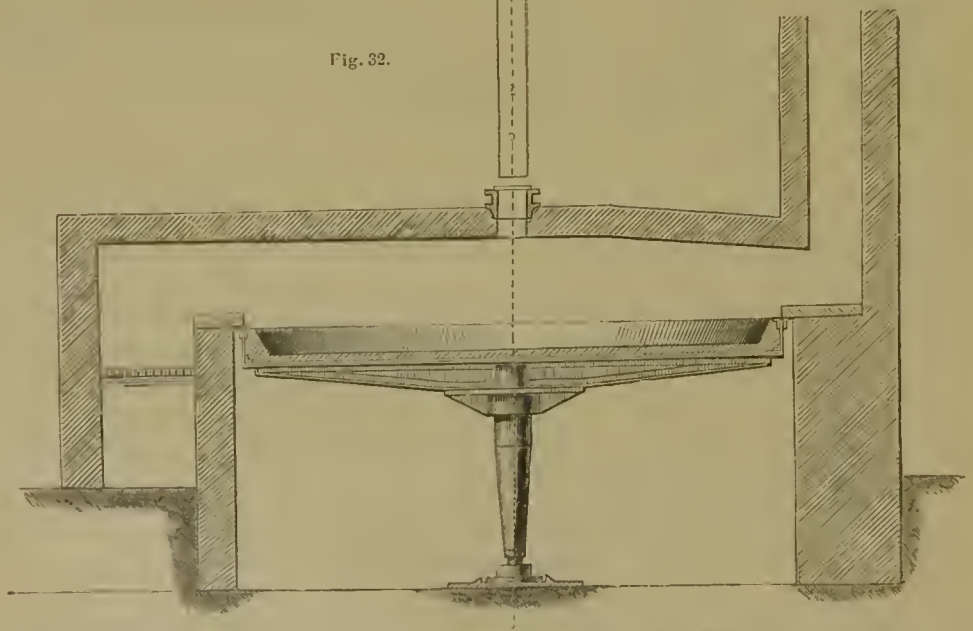



Fig. 32.



provided for discharging the ore by the revolution of the hearth, so that but little manual labour is required, except for firing. This kind of furnace is illustrated on Figs. 30 to 33, and its different parts can be easily recognized in the diagrams. The diameter of the pan, *a*, forming the furnace-hearth is 16 feet;

it is lined with firebricks and carried by radial girders, *b*, attached to a vertical shaft, *c*. The pan revolves round its vertical axis by means of an endless chain, *f*, running on a pulley, *g*, underneath the pan, and set in motion by suitable gearing from a horizontal shaft, *h*, running outside the furnace. From the same shaft is derived the reciprocating motion of the plough, *n*, working inside the furnace, by means of the cross-head, *r*, and the rod, *o*, and the gearing *m*, *i*, *p*. The gearing is so arranged that, during each revolution of the pan, the plough is only moved forward or backward to the extent of its own width, so that every part of the hearth is worked up by it. The diagrams also show the charging hopper, *s*, and the discharging plates, *t*, which are let down by means of a chain and pulley whenever it is time to discharge the furnace; they are so arranged that they throw the ore towards the circumference of the pan, and ultimately out of it through a shoot, *v*, on to the floor. As soon as this is completed they are drawn up again, and the opening through which they had passed is closed by a damper.

Fig. 33

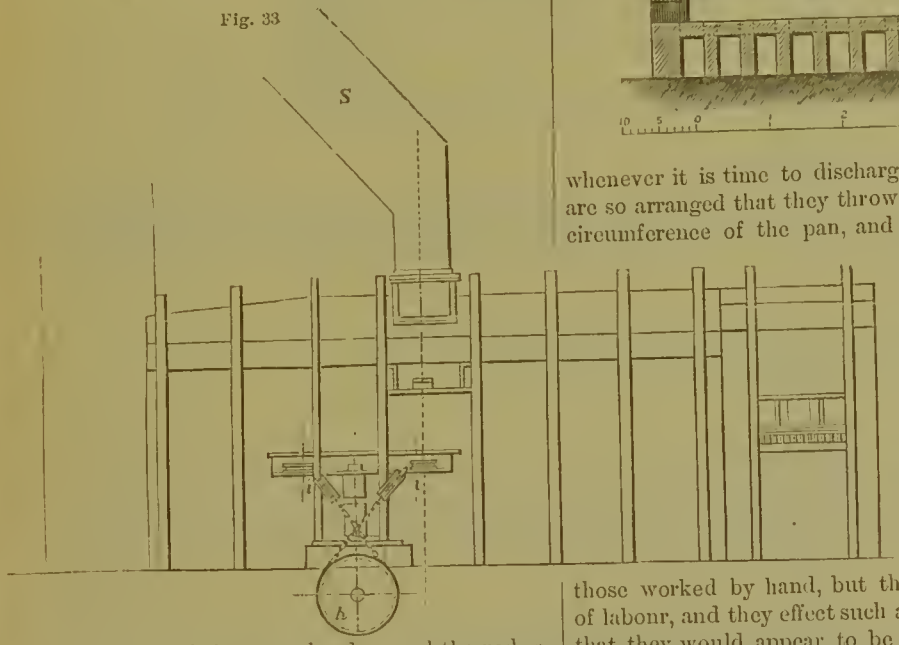
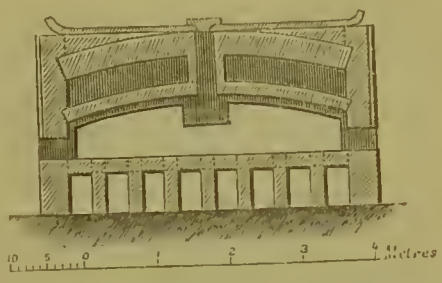
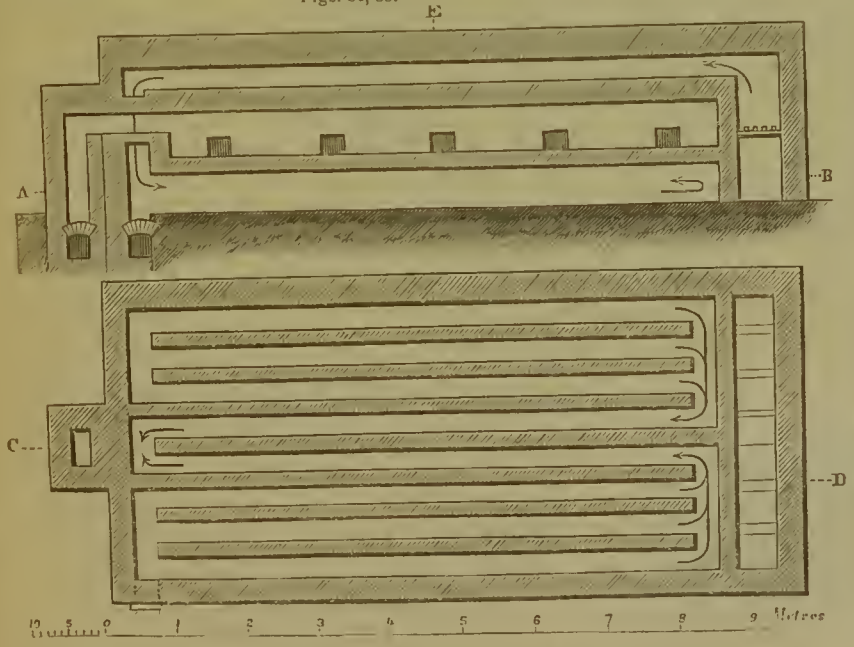



Fig. 36.




These furnaces are, of course, much more expensive than those worked by hand, but they save a great deal of labour, and they effect such a complete calcination that they would appear to be the most efficient of all. There are twelve of them in use at the Bede Metal Works at Hebburn-on-Tyne.

Figs. 34, 35.




3. *Close Furnaces.*—In these the flame is not in direct contact with the ore, but the latter is heated by a large muffle through the brick work; the fire passes both over the arch forming the roof and under the bed forming the bottom of the muffle, and the air required for oxidation only enters through the working doors. This kind of furnace is used at all the works owned by the Tharsis Sulphur and Copper Company, and is shown in Figs. 34, 35, 36. Fig. 34 is a longitudinal section on line of C—D (Fig. 35); Fig. 35, a plan on line of A—B (Fig. 34); and Fig. 36, a cross section on line E—F (Fig. 34).

4. *Combined Furnaces*, in which the bed for one half of its length is protected by a curtained arch, so that the bed remote from the fire can be kept at

a fair working heat without overheating the bed nearer the bridge. In this furnace the flame, after passing over the working bed, returns under it in flues, over which the bed is formed by tiles. These furnaces are about 20 feet long and 9 feet wide; they are in use at the Bede Metal Works, and are also shown on Figs. 37, 38, 39, 40. Fig. 37 is an elevation; Fig. 38, longitudinal section; Fig. 39, a plan of working bed level; and Fig, 40, a cross section on line, A—B, Fig. 39.

Fig. 37

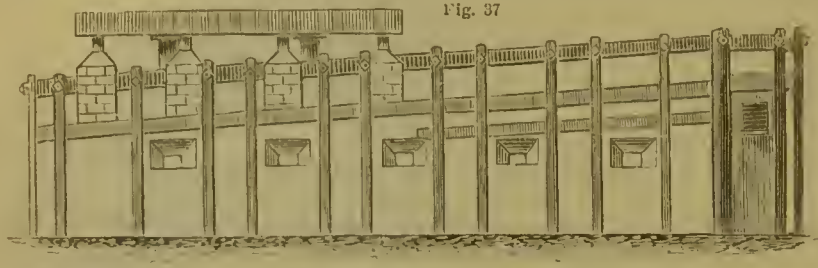


Fig. 38.

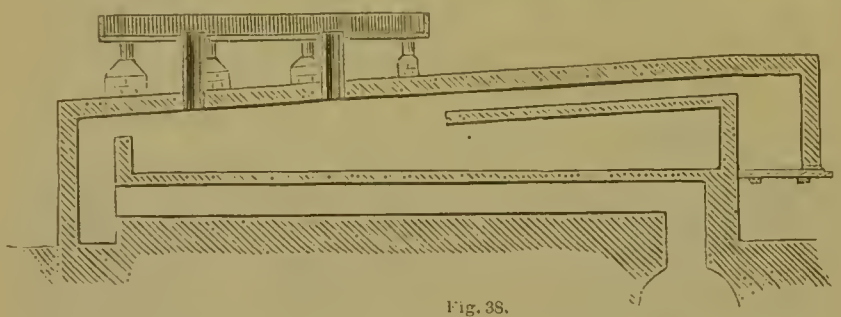


Fig. 39.

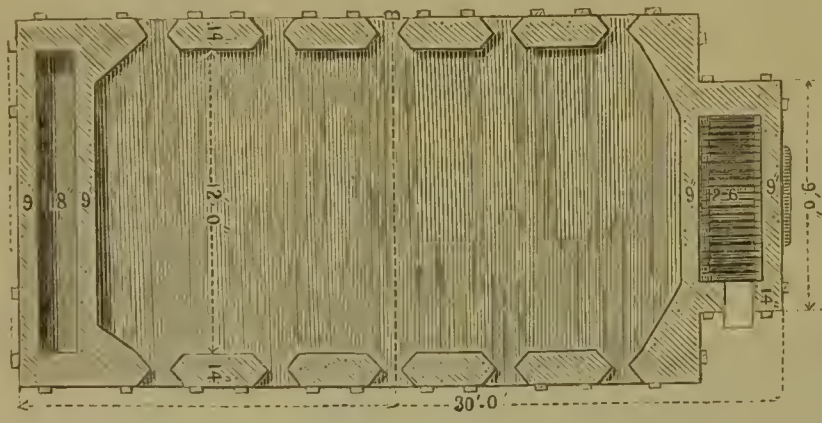
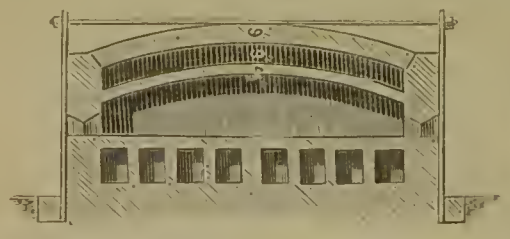



Fig 40.



5. *Open Reverberatory Furnaces*, about 30 feet long by 11 feet wide, heated by gas produced in Siemens' generators; the gas is burnt first in flues under tiles forming the bed of the furnace, and after this the flame is carried over the same bed in direct contact with the ore. These furnaces are used by the Widues Metal Company and several other firms in Lancashire and Cheshire; they are shown in the diagrams, Figs. 41, 42, 43, 44. Fig. 41 is a longitudinal section on line C—D (Fig. 42); Fig. 42, a plan on line A—B (Fig 41); Fig. 43, a front elevation; and Fig. 44, a back elevation.

Whatever furnace may be used, the object of the operation is always that of oxidizing the burnt ore completely, in such a manner that the copper is as much as possible converted into sulphate, which is further converted into chloride by means of the rock salt, sodium sulphate being produced at the same time. Experience has shown that mere calcining, without sodium chloride, never renders the whole or even the larger portion of the copper soluble (as sulphate). Even in calcining with salt a certain portion of the copper always remains as oxide; but the largest portion of this is recovered by using hydrochloric acid in the subsequent lixiviatiou.

The following table gives a good idea of the result of the calcination, according to Gibb's analyses:—

| | Gas Furnace. | | Close Furnace. | | Mechanical Furnace. | |
|---|---|---|---|---|---|---|
| | P. cent. | Cu. P. cent. | P. cent. | Cu. P. cent. | P. cent. | Cu. P. cent. |
| Cupric chloride,.. | 4·03 | = 1·90 | 4·25 | = 2·00 | 6·70 | = 3·15 |
| Cuprous chloride,.. | ·32 | = ·20 | ·35 | = ·21 | nil. | |
| Cupric oxide.... | 1·26 | = 1·00 | ·88 | = ·70 | ·32 | = ·25 |
| Sodium chloride,.. | 2·50 | | 3·40 | | 0·90 | |
| Sodium sulphate,.. | 13·18 | | 17·40 | | 14·03 | |
| Insoluble copper,. | | ·15 | | ·12 | | ·13 |
| Total copper,.... | | 3·25 | | 3·03 | | 3·53 |

The main point to be observed is always that as little as possible of the copper should remain insoluble in water and dilute acid; in the above

samples this amounts to ·12 to ·15 per cent. on the burnt ore; but when using ores rich in copper or badly burnt, the proportion of insoluble copper becomes much greater and the loss more serious. It is contended for the close furnace that the proportion of insoluble copper is rather less than with open calciners; but this seems to be more than compensated by a greater expenditure of fuel. The greatest advantage is attained by the mechanical furnace; this is easy to understand, as the best calcination should combine an equable low red heat with continual stirring, in which respect no furnace can compare with Gibb and Gelstharpe's. With this furnace next to no cupreous chloride is formed, and the proportion of cupric oxide, however refractory, badly burnt, or rich in copper the ores may be, rarely exceeds $\frac{1}{4}$th per cent.

Fig. 41.

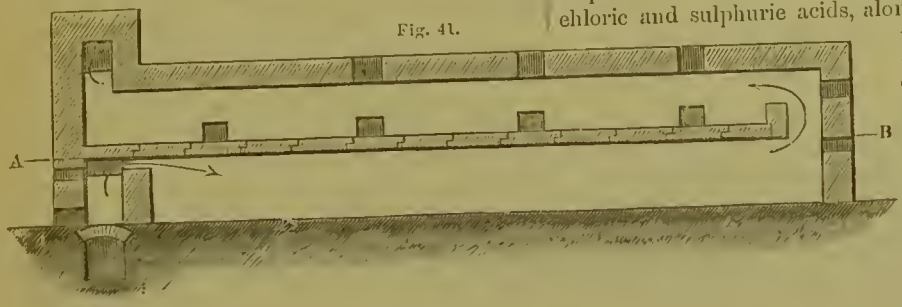
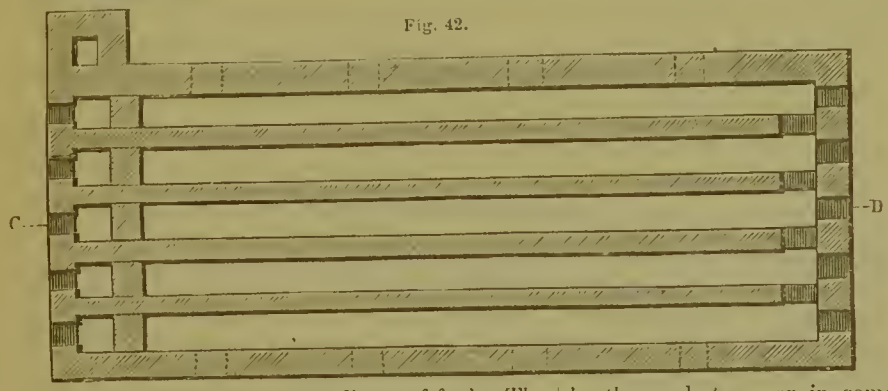



Fig. 42.




The usual weight of the charges is: for the mechanical furnaces, 5 tons of ore (time of calcining, nine hours); for the open furnace with curtain arch, 56 cwts. (time of calcining, eight hours); for the gas furnace, about the same; the close calciners take more time.

During the calcination a great deal of gas is evolved, principally sulphurous and sulphuric anhydride, hydrochloric acid, and chlorine. These are mixed with the gas from the fire, except in the case of close calciners, and they are passed through condensing towers packed with coke, over which a constant stream of water is kept running, exactly similar to those used in the manufacture of sodium sulphate. The result is a mixture of dilute hydrochloric and sulphuric acids, along with a small proportion of volatilized metallic chlorides. These are not lost, as the liquid from the condensers is very usefully employed in the subsequent process of lixiviation, when its acids reduce the larger proportion of the cupric oxide to the soluble state.

The next step in the process is the *lixiviation* of the calcined mixture. It is carried out in square wooden tanks, 10 to 12 feet square and 4 feet deep, in which the ore is placed on a filter formed of heather and straw, or in some similar way, by successive washings with hot water, which in percolating the ore dissolves the soluble salts. The water is followed by the weak acid from the condensers, or if this should not be sufficient, by ordinary hydrochloric acid, and finally hot water is used again till the ore is exhausted. It is usual to pump up (or preferably, to blow up by means of an injector) the last washings of one set of tanks to serve for the first washings of the next set, in order to obtain a more concentrated solution of copper. The solutions contain, besides copper and other salts, also silver and gold, which are sometimes recovered by special processes, as will be mentioned hereafter. Arsenic, bismuth, and lead are also present, partly dissolved out of the calcined ore, and partly from the acid used in lixiviation, more particularly when the acid condensed from the calcining furnace gas has been employed for this purpose.

Fig. 43.

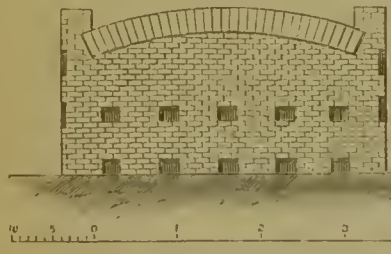
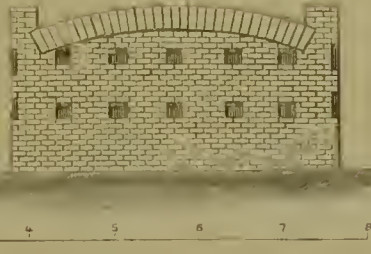


Fig. 44.




It is the value of the residue from the lixiviation which makes the wet copper process more economical than the dry processes for poor cupreous ores; since it constitutes an iron ore of considerable value, known as "purple ore," or sometimes as "blue

billy." Mr. Gibb gives the following analysis of two fairly typical specimens:—

| | | | |
|---|---|---|---|
| Ferric oxide, | 90·61 | .. | 95·10 |
| Copper, | ·15 | .. | ·18 |
| Sulphur, | ·08 | .. | ·07 |
| Phosphorus, | Nil | .. | Nil |
| Lead sulphate, | 1·46 | . | 1·29 |
| Calcium sulphate, | ·37 | .. | ·49 |
| Sodium sulphate, | ·37 | .. | ·29 |
| Sodium chloride, | ·28 | .. | — |
| Insoluble residue, | 6·30 | .. | 2·13 |
| | 99·61 | .. | 99·55 |
| Metallic iron, | 63·42 | .. | 66·57 |

This ore, it will be observed, is almost entirely free from sulphides and entirely so from phosphorous, and very rich in iron; its only drawback is this, that it is in the state of powder, which greatly militates against its use in the blast furnace. It has been attempted to mould it into bricks of sufficient coherency to allow of their being introduced into the blast furnace, but this raises the cost too much; in some cases it is also used direct in its pulverulent state in the blast furnace, but its main employment is for "fettling" the hearths of puddling furnaces, for which object it is eminently adapted and mostly used. Its direct conversion into malleable iron or steel has not yet been carried out successfully on a large scale.

The liquors obtained by lixiviating the calcined ores must now be submitted to the process of *precipitation*. It will, however, be useful to first give a table showing the action of water and dilute acid on the calcined ores, according to Mr. Gibb; this table will at the same time show the great difference between the mechanical and the hand-worked furnaces:—

| | Mechanical Furnace. | | Hand Furnace. | |
|---|---|---|---|---|
| | | Per cent. Cu. | | Per cent. Cu. |
| *Soluble in Water*— | | | | |
| Cupric chloride, | 4·16 | 1·96 | 3·81 | 1·82 |
| Cupreous chloride, | Nil | — | ·19 | ·12 |
| Cupric sulphate, | 1·83 | ·81 | Nil | — |
| Ferrous sulphate, | ·15 | — | Nil | — |
| Ferric sulphate, | ·75 | — | Nil | — |
| Zinc sulphate, | 2·01 | — | 1·95 | — |
| Calcium sulphate, | 1·29 | — | 1·39 | — |
| Sodium sulphate, | 9·17 | — | 11·13 | — |
| Sodium chloride, | Nil | — | 2·61 | — |
| *Soluble in dilute hydrochloric acid*— | | | | |
| Cupreous chloride, | ·015 | ·10 | ·33 | ·21 |
| Cupric oxide, | ·225 | ·18 | 1·01 | ·81 |
| Lead sulphate, Ferric oxide, | Not estimated | | Not estimated | |
| *Residue* (by difference) = purple iron, | 80·40 | ·08 | 77·55 | ·11 |
| | 100 00 | 3·01 | 100·00 | 3·07 |

The fact that the more complete action of the mechanical furnaces produces almost pure sodium sulphate (free from chloride) induced Mr. Gibb to propose a most ingenious plan for utilizing the same, which unfortunately has never been carried out to a commercially successful end, although it was at work on a very large scale for some time. It consisted in precipitating the copper liquors by means of sulphuretted hydrogen obtained in a subsequent stage of the process; the cupric sulphide was separated by a filter press and smelted in the usual way. The acid liquor remaining was boiled down to dryness, the residue mixed with small coals and furnaced, by which means the sodium sulphate was almost entirely reduced to sulphide; the furnaced mass was lixiviated with warm water and the solution treated with carbonic anhydride, produced by the burning of coke; the sulphuretted hydrogen evolved in the operation was utilized for precipitating the copper liquors, as mentioned above, and the remaining solution of sodium carbonate was boiled down to dryness and calcined in the usual way, thus yielding commercial soda ash. This process having been given up, there is at present no process actually at work for utilizing the sodium sulphate in the copper liquors, or for precipitating them in any other way than by means of *metallic iron*. This is usually employed in the form of scrap iron, but for this can be substituted with very great advantage the "spongy" iron, obtained by reducing purple ore with coal in a specially constructed furnace, which is shown in Plate I., Copper. The flame heats the mixture both from underneath, through the bed constructed of tiles, and by direct contact from above. The furnace has a very deep hearth, and its working doors are usually kept tightly luted, to avoid the re-oxidation of the reduced iron; the process of reduction lasts from nine to eighteen hours, and after its termination the ore is drawn into air-tight boxes, by means of iron pipes passing through the furnace bed and the flues underneath into a place provided for the purpose. The boxes are immediately closed, and only opened when their contents are completely cooled down, so that the spongy iron is not subject to instant re-oxidation, as it would be if exposed to the air in the hot state. It is ground to powder and effects the precipitation of the copper almost instantaneously, whilst scrap iron takes a long time to perform its work. The following are analyses (by Gibb) of copper precipitate obtained by various kinds of iron, so far as the most important constituents are concerned:—

| | Precipitated with | | |
|---|---|---|---|
| | Spongy Iron. | Heavy Scrap. | Light Scrap. |
| | Per cent. | Per cent. | Per cent. |
| Copper, | 67·50 | 72·50 | 67·50 |
| Arsenic, | ·137 | ·306 | ·100 |
| Silver, | ·011 | ·046 | ·066 |
| Lead, | 1·30 | 2·60 | 1·74 |
| Ferric oxide, | 5·15 | 4·41 | 7·56 |
| Carbon, | 5·10 | — | — |
| Silica, | 3·20 | — | — |

This precipitate is either sold to copper smelters, who smelt it advantageously with copper regulus, or it is smelted by itself in the extracting works. In the latter case it is charged into reverberatory furnaces, similar in every way to the ordinary copper-smelting furnaces. When run down the slag is skimmed off and the copper tapped into sand pig moulds as blister copper. When, however,

spongy iron has been used, the carbon in excess prevents the copper being melted directly to blister, and about one half of the precipitate is therefore calcined in large calciners, exactly like those used for calcining burnt ore with salt. The carbon is here burnt off and the copper partially oxidized; the product is mixed with raw precipitate, and can now be smelted as usual. The slag is skimmed off and the copper tapped as blister. The slag contains from 3 to 10 per cent. of copper, which are recovered by smelting with raw ores, producing "coarse metal" (sulphide of copper and iron containing about 30 per cent. of copper), and this is brought forward to copper by calcining, smelting, and washing in the ordinary way. The blister copper made from the precipitate is refined by roasting, to oxidize the iron, sulphur, &c., which it may contain, followed by reduction of the cupric oxide produced in roasting by charcoal, and poling in the way usually employed by the copper smelter.

The copper produced is pure and tough, and an easily marketable article. The following analyses will show its impurities compared with those of English copper made by the ordinary mode of smelting:—

| | Copper from Wet Process. | | "English" Copper. Field's Analyses. | |
|---|---|---|---|---|
| | Per cent. | Per cent. | B. S. Per cent. | Tough. Per cent. |
| Silver, | ·022 | ·016 | ·035 | ·047 |
| Arsenic, | ·030 | ·170 | ·105 | ·090 |
| Antimony, | none. | trace. | ·010 | trace. |
| Bismuth, | ·006 | ·019 | ·035 | ·130 |
| Lead, | none. | ·002 | none. | — |

*Treatment for Silver.*—It has been mentioned above that the solutions obtained in lixiviating calcined ores contain silver and gold, certainly in very small quantities, viz., about 14 dwts. of silver and 2 or 3 grains of gold to the ton of burnt ore. But even these proportions, especially that of the silver, are not too small to prevent the precious metals from being recovered, and two methods are actually in use for this purpose at this moment.

That of Claudet, used by the Widnes Metal Company, Lancashire, is founded upon the insolubility of silver iodide in solutions of chlorides. The copper liquor, previously to being precipitated with iron, is run into separate vessels, where a solution of potassium iodide, exactly equivalent to the silver present, is mixed with it and allowed to stand for two or three days. The silver iodide is precipitated, and settles at the bottom of the tank; the clear liquor is run off to undergo the iron treatment, and fresh liquor direct from the lixiviating tanks run into the desilverizing tank, to be treated with iodide. The silver iodide, accumulated by a number of successive precipitations in the same tank, is removed, washed, and decomposed by metallic zinc; this results in the formation of metallic silver and of zinc iodide, the latter being available for further operations in the place of potassium iodide. The silver is certainly not pure, but in the form of a residue containing 5 to 6 per cent. of metallic silver and about ·06 per cent. of gold, the bulk of it being lead, zinc oxide, calcium sulphate, &c. Only the first three washings of the burnt ore are submitted to Claudet's process, as they contain 95 per cent. of the silver.

Gibb's process depends on the fact that, when sulphuretted hydrogen is passed through a copper solution containing a small proportion of silver, the latter metal is at first precipitated in a much larger proportion than the former; when 6 per cent. of the copper have been precipitated, the great bulk of the silver has also been thrown down as sulphide, and is therefore concentrated in the upper precipitate. The sulphuretted hydrogen is generated by the action of hydrochloric acid on the "tank waste" of alkali works, and blown into wooden tanks containing the copper solution, along with a large quantity of air purposely drawn in for dilution, generally for twenty minutes, till by a rough testing (with potassium cyanide) it is ascertained that 6 per cent. of the copper are precipitated. Whilst the copper obtained without any desilverizing process contains on an average 20 ozs. silver per ton, the 6 per cent. precipitated as above contain 200 ozs. silver per ton of copper; the copper made from the residual liquid only contains 3 ozs. silver per ton. The precipitate of cupric and argentic sulphide is washed and pressed in a Needham's filter press; it is then calcined at a low temperature in a furnace exactly similar to those serving for the calcining of burnt ores with salt. In this operation chlorides of silver and copper are produced with oxide and sulphate of copper. The calcined precipitate is ground to a coarse powder and lixiviated; the cupric sulphate is dissolved along with a mere trace of silver (1 oz. per ton) and added to the ordinary copper liquors. The residue remaining in the lixiviating vessel is now treated with a hot solution of common salt, which dissolves out the silver chloride, along with some copper and lead; the residue only contains from 3 to 4 ozs. of silver per ton of copper, and is smelted as usual. The solution of chlorides is mixed with milk of lime, which precipitates all the metals; the precipitate is well washed, to free it from calcium chloride, and then digested with dilute sulphuric acid to dissolve the copper, and again washed. After drying the residue has the following composition:—

| | |
|---|---|
| Silver, | 8·77 |
| Lead oxide, | 28·66 |
| Cupric oxide, | 3·75 |
| Ferric oxide, | 2·61 |
| Calcium oxide, | 13·67 |
| Sulphuric anhydride, | 31·72 |
| Chlorine, | 4·70 |
| Water, | 4·20 |
| Insoluble, | 1·40 |
| | 99·48 |

It is sent to Birmingham and used by the silver smelters there. By either process about 1 part silver on 60,000 of burnt ore, equal to 2*s.* 6*d.* per ton, is recovered at a cost of about 10*d.* per ton of ore worked; and looking at the very large quantity of burnt ores worked up, this saving is not inconsiderable.

*The Lime Process.*—A scheme has lately been put forward under this name for the treatment of the poorer ores of the Snowdon Copper Mining Co., which requires to be tested by experience before much can be said of its merits. The ore is crushed and mixed with a small quantity of lime, and made up into cakes of a convenient shape for stacking in a kiln; these are then burnt at a low red heat with but little expenditure of fuel; the roasted ore being crushed and lixiviated with either water or an acid liquor collected from the kilns. The copper is said to be converted from its original form of sulphide to sulphate of copper, which is soluble; from the solution copper sulphide can again be obtained by means of sulphuretted hydrogen, the difference being that it is now concentrated, and in a form from which the copper may easily be smelted.

Copper Assaying: Dry Way.—For the purposes of assaying copper ores may be divided into four classes. These may usually be distinguished by inspection, or a sample may be washed and by that means the composition approximately guessed at. On the determination of the class of ore it belongs to will depend its treatment in the assaying. The following are the classes:—

*First Class.*—Native copper, which only requires to be remelted to be fit for the market.

*Second Class.*—Ores not containing sulphur, namely, oxides, carbonates, silicate, and chloride; these require simple reduction and the refining of the coarse metal reduced.

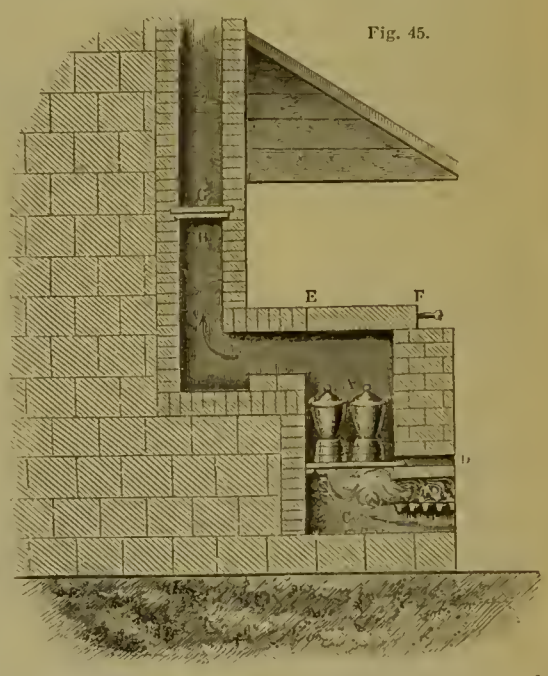
*Third Class.*—Ores containing sulphur, but with a large percentage of copper and not much iron. These require to be roasted "dead," then to be fused for the reduction of the metal, this to be followed by refining of the coarse metal obtained.

*Fourth Class.*—Less rich ores, containing sulphur and iron in considerable quantity, and a large proportion of earthy impurities. To this class belong the greater part of the Cornish ores. For these an additional fusion for "regulus" is wanted, as will be shown in detail below, where the processes described apply chiefly to this fourth class, while for the three former classes some of the earlier operations should be left out as above indicated.

To conduct an assay of copper, a furnace capable of producing a high degree of heat is indispensable; one well adapted to the purpose is represented in Fig. 45. In this sketch, the space A is assigned to the fuel and crucibles wherein the reduction is to be effected; this may be 16 inches in depth, from the level of the cover, E F, to the grate, and from 8 to 10 inches in breadth. C is the ashpit, which is slightly raised from the floor-level, to facilitate the removal of the cinders; the bars of the grate are introduced through the opening, D, the further end resting upon a proper support fixed in the walls of the furnace. B is the chimney, which should be sufficiently capacious to carry off all the products of the combustion; and it should be entirely kept apart from any other opening. The draught is regulated by the damper, G, which can be pushed in or drawn out by an iron handle. The crucible and assay are introduced into the furnace at the mouth, E F, and placed upon pedestals of brickwork, resting upon the bars of the furnace, after which the opening is closed by the tile, as seen in the figure. To prevent cracks or fissures forming in the walls of the furnace, by repeated expansion and contraction of the material as it is heated, they are coated over with plates of stout sheet-iron, riveted together, and, if necessary, bound by hoops of metal.

Besides this, the most important part of the arrangements for assaying, other apparatus, none of it, however, very complicated, is required—the various utensils for holding the crucibles, for stirring the ore within them during the roasting processes, moulds in which to form the assay, &c. The best fuel to use is coke broken into pieces about the size of an egg. If the ore has less than 10 per cent. of copper, 400 grains of it are taken; for a greater percentage (10 to 30 per cent.), but 200 grains; and if still richer ores,

Fig. 45.




100 grains. The ore, finely powdered, is first roasted in a crucible at a dull red heat, being stirred continually till a portion of the sulphur is expelled; the pot is then taken from the fire, and allowed to cool gradually. If the assay has a reddish appearance on the top, and a blackish underneath, the process is properly executed. The same crucible being preserved for the next process, the roasted ore is now mixed with the fluxes—borax, lime, and fluor spar—in proportions which must vary with the samples according to the character of the earthy materials contained in the ore, and a layer of salt is put over all. A not uncommon plan is to dispense with the previous roasting, and at this stage add nitre to the previously named fluxes, this being an oxidizing agent, whose action will stand in place of that of the air. The crucible being heated gently all round by coke, which when ignited still completely surrounds it, a red heat is gradually attained and

kept up for about a quarter of an hour. When effervescence through the slag has ceased the operation is complete; the contents are then quickly poured out into an iron mould, whence they are transferred to water while still hot for the purpose of cracking the slag, and enabling it to be separated from the button of regulus. This regulus is a disulphide of copper, combined with sulphide of iron, copper being present to the amount of about 60 per cent.

The regulus is next roasted in order to dissipate all the sulphur in the form of sulphurous acid, and to bring the copper to protoxide and the iron to peroxide. For this purpose the button is ground to fine powder, and placed in a smaller crucible; several such roastings can be carried on in one furnace at the same time. The assay is heated first to a low red heat, and afterwards to a bright red heat; it is continually stirred in the early part of the operation and occasionally later on; after half an hour or so all the sulphur will have been driven off, and the calcination will be complete.

Fusion of the regulus is the next step; the object being to reduce the oxide of copper to the metallic state, and to bring the iron to such a condition (protoxide) as will enable it to be taken up by the fluxes. The flux chiefly used is a mixture of tartar and nitre with, in some cases, the addition of borax; sometimes charcoal and carbonate of soda are employed; in any case the flux must perform the two functions of reducing the oxides and dissolving the iron protoxide. The same crucible is used that the calcination was done in; a bright red heat is required; first fusion occurs, and afterwards effervescence. When the effervescence ceases the operation is complete, and all is poured together into a mould, where the button of *coarse copper* is found separate from the slag, which, however, may contain a small quantity of the metal, which can be obtained by a separate fusion, the weight being added to that of the main portion of the assay.

One more operation is, however, necessary; this is *refining* the coarse copper. The crucible used in the last operation being heated to redness the button of copper is dropped in; it soon melts and is acted on by the air so far as to have its impurities oxidized; when the surface of the melted metal has become quite bright some refining flux (a deflagrated mixture of nitre, cream of tartar, and salt) is poured on, and after a couple of minutes the whole contents are poured into a mould, and a button of *fine copper* is obtained. The slag from this, as well as the slag from the coarse copper, being now ground and melted together, with the addition of charcoal, some small beads (called *prills*) of copper will be obtained, whose weight, as stated above, must be added to that of the larger button.

It will be seen that this long process of assay is but a rehearsal, so to say, on a small scale, of the Swansea copper smelting. The results it gives are quite comparable with the yield that may be expected in the smelting itself, the sources of error being similar in both operations: hence it is the universally accepted mode of testing copper ores followed by practical men. Chemical processes are far more accurate; but dry assay shows not the true amount of copper contained in an ore, but the true amount which can be extracted from it by smelting.

*Copper Assaying: Wet Way.*—The process used at the Mansfield Copper Works is as follows (according to Thorpe):—About 5 grms. of the finely powdered ore are weighed out into a flask and mixed with 40 c.c. of hydrochloric acid of about 1·16 spec. grav., 6 c.c. dilute nitric acid (made by mixing equal bulks of water and pure acid of spec. grav. 42) are added, and the flask is gently heated for thirty minutes on a sand bath, after which it is boiled for fifteen minutes. The whole of the copper is now in solution; the extraction is complete, even in the case of very rich ores, provided sufficient attention has been paid to the powdering. The solution is filtered into a large beaker, into which a rod of zinc, weighing about 50 grms. and surrounded with a piece of thick platinum foil, has been previously placed. It is necessary that the zinc employed should be as free as possible from lead. The precipitation of the metallic copper commences immediately, and is generally complete in about half an hour. The rod of zinc is withdrawn, and the precipitated copper repeatedly washed by decantation. If the amount of the copper does not exceed 6 per cent. (which may be approximately known from the bulk of the reduced metal) it is dissolved in 8 c.c. of the dilute nitric acid, prepared as above. The beaker is gently warmed, and the amount of copper in the liquid titrated by a solution of potassium cyanide, after previous addition of ammonia solution, prepared by diluting 1 volume of ammonia-water (sp. gr. 0·93) with 2 volumes of water. When the amount of copper in the ore exceeds 6 per cent., the metal is dissolved in 16 c.c. of the nitric acid solution, and the liquid is washed into a 100 c.c. flask, diluted to the mark, shaken, 50 c.c. withdrawn, mixed with 10 c.c. of the dilute ammonia, and titrated with potassium cyanide, according to Parkes' process.

When a solution of potassium cyanide is mixed with an ammoniacal solution of cupric sulphate or nitrate, the azure colour gradually disappears with the formation of copper-ammonium cyanide, free ammonium cyanide, ammonium formate and urea. The reaction is only constant so long as the amount of free and combined ammonia present is invariable.

The strength of the solution of the potassium cyanide is tested thus:—Exactly 5 grms. of chemically pure copper, prepared by the electrotype process, are weighed out into a litre flask and dissolved at a gentle heat in 266·6 c.c. of the nitric acid, prepared as above. On cooling, the solution is diluted to the mark; 30 c.c. of this solution, containing 0·15 grms. of metallic copper, are placed in a beaker and mixed with 10 c.c. of the dilute ammonia liquid, and the solution of potassium cyanide is added from a burette, with constant stirring, until the blue colour of the liquid just disappears. The strength of the cyanide should be

so arranged that 1 c.c. of the solution is equivalent to 5 milligrammes of copper.

The titration of the solution of the sample of ore is made in exactly the same manner. If exactly 5 grms. have been taken, and the cyanide is of the above strength, each cubic centimètre of the solution required for decolorisation is equivalent to 0·1 per cent. of copper. The number of cubic centimètres needed, divided by 10, gives the percentage of copper at once.

This method is very expeditious and at the same time accurate, if due care be exercised, and if the titrations are always made under similar circumstances. The presence of a very small quantity of lead, arsenic, or antimony, does not influence the results, but zinc, nickel, and cobalt are more injurious. The precipitated copper must, therefore, be washed thoroughly before dissolving it in nitric acid. The solutions must be quite cold before titration, since less potassium cyanide is needed to decolorise a solution when warm than when cold. The standard solution of potassium cyanide requires to be titrated from time to time, since its strength is not invariable.

Another method is the Swedish one, precipitating the copper by metallic iron and weighing it. The presence of any metal not precipitable by iron is of no consequence in this case; nor is that of lead, tin, and antimony, which remain behind in dissolving, but arsenic must be separated as sulphide. The ore is decomposed with aqua regia, sulphuric acid is added, and the whole evaporated till all nitric acid is driven off; the residue is dissolved in water with a few drops of sulphuric acid and filtered; a few pieces of clean iron wire are added, and the whole gently heated. The copper is precipitated in a spongy form; it is washed off the iron, the liquid part decanted along with any carbon from the iron floating in it, and the copper gently dried and weighed. This process becomes much more exact by using pure zinc in the place of the iron, but it takes much longer time in that case; on the other hand, Luckow has described a process for separating the copper by the galvanic current, which is done very quickly and produces it in a consistent and not easily oxidisable form.

A very exact mode of wet assay for copper is the precipitation as sulphide by sulphuretted hydrogen or sodium hyposulphite; the cupric sulphide is ignited with exclusion of the air, and thus converted into cuprous sulphide ($Cu_2S$), 100 parts of which contain 79·85 per cent. of copper. All metals which are not precipitated from their acid solutions by sulphuretted hydrogen are quite harmless in this case, as well as lead which remains behind in dissolving; mercuric and arsenic sulphide are volatilized in igniting, and only antimony and tin, if present, require a special treatment.

The same precipitation has been utilized by Pelouze for a volumetrical estimation of copper in an ammoniacal solution, by means of a solution of sodium sulphide. The latter is run from a burette into the copper solution heated to 65° to 85° C., at which temperature a constant compound ($5\,CuS + CuO$) is formed. The end of the reaction is recognised by the extinction of the blue colour of the solution. Zinc, antimony, arsenic, &c., are only precipitated after the copper, and are therefore not injurious. This assay is not quite so convenient as Parkes' method with potassium cyanide, and the test solution is much more variable. In the actual practice of copper works in this country Parkes' method (of which the Mansfield process described in the beginning is only an application) is that mostly employed.

**COPPER ALLOYS.**—Copper is probably capable of entering into combination with all the metallic elements severally, compounds being formed differing in character from their constituents. The contamination of copper with even very small quantities of some metals, such as zinc, iron, bismuth, and arsenic, materially alters its physical properties, rendering it a less perfect conductor of heat and electricity, and impairing its malleability and tenacity.

Potassium and sodium were formerly believed to increase the malleability of copper in a high degree. Dumas suggested the addition of cream of tartar to the fused metal as a means of producing it, and produced an alloy having the following composition:—

| | Centesimally. |
|---|---|
| Copper, | 99·12 |
| Potassium, | 0·38 |
| Calcium, | 0·33 |
| Iron, | 0·17 |
| | 100·00 |

Karsten states that copper thus treated only takes up 0·13 per cent. of potassium, and becomes less ductile; while according to Serullas copper does not alloy with cream of tartar when heated to redness.

Manganese forms many alloys with copper. They greatly resemble the bronzes; are very hard and sonorous, and melt very readily. The alloy containing 15 per cent. of manganese is grey, very hard and brittle, melts like bronze, may readily be cast, and does not alter much on keeping. Alloys containing less than 12 per cent. are ductile, and may be hammered into thin sheets. Manganese alloys are of a reddish colour, and become covered with a greenish tarnish when exposed to damp air.

With cobalt, copper forms ductile and malleable alloys, which melt at about the fusing point of copper.

An alloy of copper with aluminium, consisting of 10 parts of aluminium with 90 parts of copper, is known as aluminium bronze. It is a definite chemical compound, having the composition $Cu_9Al$. Being of a beautiful golden colour, capable of taking a high polish and little liable to oxidize, it is much used as a substitute for gold. Aluminium bronze is tough and hard, and at the same time very malleable. The affinity of aluminium and copper for each other is so great that plates of the two metals bound together, after having their surfaces well cleaned, can be welded by exposing them to a low red heat.

In 1858 a process was patented for making aluminium bronze by heating together a mixture of

oxide of copper, alumina, and carbon in the proper atomic proportions, the carbon being slightly in excess.

Iron is difficult to alloy with copper, but still compounds of this nature can be made.

The two metals alloy in all proportions. The copper is melted first, and the iron added by slow degrees. The colour of the alloy deepens until the metals are equal in quantity, after which each successive addition of iron renders the colour paler. An alloy containing 2 parts of copper with 1 of iron has very great tenacity; after this, addition of iron increases the hardness but diminishes the toughness. The presence of carbon prevents the combination of the metals. Mushet produced copper-iron alloys by fusing together the sulphides of the metals.

The principal part of the *black copper ore* already described is composed of copper and iron. A mixture of 100 parts of grey cast iron and 5 of copper yields an alloy of considerable hardness, which has been proposed as a material for anvils.

The presence of iron renders copper brittle and of a coarse grain; on the other hand, it was found by Faraday that even a trace of copper injures the quality of steel, and that in the proportion of 2 per cent. it renders it brittle; and Mushet states that it affects cast iron likewise.

The alloys of copper with cadmium, lead, antimony, and arsenic, have been hitherto of little use.

The most valuable alloys of copper are its combinations with zinc, tin, nickel, gold, and silver.

The term alloy was at one time exclusively applied to mixtures of metals with gold and silver, but in chemistry it now means the chemical combination of any two or more metals, or their solution in one another. The combinations of mercury are still known as *amalgams*. Alloys possess all the physical and chemical characteristics of metals; they have metallic lustre, are more or less ductile, malleable, elastic, and sonorous, and conduct heat and electricity. Though retaining these properties, the compound is often so modified in each of them that it does not resemble either of its constituents, and might consequently be regarded as a new metal, having distinctive characters peculiar to itself.

Many alloys consist of simple elements in definite or equivalent proportions, whilst others are produced from compound bodies; and often the components do not exist in the ratio of their chemical equivalents. Metals, in forming alloys, do not, however, combine indiscriminately with one another; the union is governed by the greater affinities which some of them manifest for each other. This all tends to prove that chemical combination is exercised, and that the alloys are not merely mechanical mixtures, but definite chemical compounds. Many of the alloys which have been hitherto examined corroborate this fact; and it is probable that peculiar properties belong to the combination when prepared in atomic proportions, such as is done in making the superior quality of brass. It is remarkable, also, that the native gold found in auriferous sands and rocks is alloyed with silver in the ratio of 1 equivalent of the latter to 4, 5, 6, 8, 10, &c., equivalents of the former; but the combinations never afford results indicative of the metals being united in fractional parts of an equivalent. Another evidence of the chemical combination subsisting is, that the compound melts at a lower temperature than the mean of the fusing points of its ingredients. An instance very remarkable in itself is the alloy of 8 parts of bismuth, 5 of lead, and 3 of tin; this compound fuses at the temperature of boiling water, although the the melting point deduced from the mean of its constituents is 514° Fahr. Thus iron, when alloyed with gold, enters into fusion at nearly the melting point of the latter metal, although when alone it is one of the most infusible elements. It is very probable that the true chemical alloy is often dissolved in excess of the free metal, and in this way evades recognition.

Again, as the melting point of the alloys differs from the mean of their constituents, so also, when the affinity between the metals is very great, the compound is generally denser than the mean, and *vice versâ*, as exemplified by the following compounds:—

| Alloys, the density of which is greater than the mean of their constituents. | Alloys, the density of which is less than the mean of their constituents. |
|---|---|
| Gold and zinc. | Gold and silver. |
| Gold and tin. | Gold and iron. |
| Gold and bismuth. | Gold and lead. |
| Gold and antimony. | Gold and copper. |
| Gold and cobalt. | Gold and iridium. |
| Silver and zinc. | Gold and nickel. |
| Silver and tin. | Silver and copper. |
| Silver and bismuth. | Iron and bismuth. |
| Silver and antimony. | Iron and antimony |
| Copper and zinc. | Iron and lead. |
| Copper and tin. | Tin and lead. |
| Copper and palladium. | Tin and palladium. |
| Copper and bismuth. | Tin and antimony. |
| Lead and antimony. | Nickel and arsenic. |
| Platinum and molybdenum. | Zinc and antimony. |
| Palladium and bismuth. | |

Crookewitt gives the specific gravities of alloys of copper with tin, zinc, and lead, as being modified as follows:—

| | Sp. gr. | | Sp. gr. |
|---|---|---|---|
| Cu, | 8·794 | $Cu_2Zn_5$, | 7·939 |
| Sn, | 7·305 | $Cu_3Zn_2$, | 8·224 |
| CuSn, | 8·072 | $Cu_2Zn$, | 8·392 |
| $Cu_2Sn$, | 8·512 | Pb, | 11·354 |
| $Cu_2Sn_5$. | 7·652 | $Cu_2Pb_3$. | 10·753 |
| Zn, | 6·860 | CuPb, | 10·375 |

Hatchett found in his experiments on alloys of gold with silver, copper, lead, and antimony, of the standard proportion, that after long fusion and casting them in vertical ingots, the analysis of the several parts of these showed that the composition was not homogeneous, but that the top portion of the bar (corresponding to the metal which was in bottom of the crucible) contained more gold than the other parts. This is the case in every instance where there is a great difference in the gravity of the constituents of the alloy, unless great pains be taken to cause the metals to combine more perfectly; because, during the fusion, the chief portion of the heavy metals will assume a level in the crucible in the order of their respective densities, unless they are prevented from doing so by stirring with a porcelain

rod. A partial separation of the metals takes place sometimes in the casting, even when all the attention possible may have been bestowed on the alloy during its formation; this is more especially the case if the casting be large and slow in cooling. The remedy for this is to fuse the ingots again, and after this the mixture will be found nearly homogeneous.

The tenacity of metals is generally increased by combining them together. Thus, an alloy of 12 parts of lead with 1 part of zinc has twice the tenacity of zinc.

Alloys oxidize more readily than their constituents do when separate. An alloy of lead and tin when heated to redness will continue to burn for some time, so rapidly does it absorb.

Alloys can only be formed by fusion; and since many of the metals oxidize with great readiness at the melting points, precautious have to be taken to stop this action, as otherwise the metals would not "wet" each other, their oxides forming a barrier.

For lead and tin resin or grease is commonly used to coat the surface; for tin and iron, sal ammoniac, &c. When more than three metals are to be combined it is found best to alloy them in pairs, and then to melt the pairs together. Brass, for instance, is improved for turning by the addition of 2 to 3 per cent. of lead. This, however, cannot be added directly, but has to be first run with the zinc and this alloy added to the melted copper.

Great art is required in the preparation of alloys, especially when they contain more than two metals; for it is not uncommon to observe two alloys of exactly the same composition differ very materially in properties, in consequence of a difference in the mode of preparation. This change often arises from the application of a higher temperature than usual, or from the order in which the fusion of the components is effected; to these points attention will be directed as the several compounds are described, and more especially in regard to the alloys of copper, which subject will now be resumed.

BRASS.—*Laiton, cuivre jaune*, French; *Messig*, German.—It would appear that no metallic compound was in more general use with the ancients than brass, it being apparently the best known to them. Tubal-cain is described as a worker in brass—copper (?) From the writings of Moses and Ezekiel also, the general use of brass is inferred, although it was evidently ranked in value far below silver and gold, as appears from the following passage, which also touches on other matters relating to ancient metallurgy:—*The house of Israel is to me become dross; all they are brass, and tin, and iron, and lead, in the midst of the furnace; they are even the dross of silver.*

Pliny says that a flourishing trade in brass was carried on in Rome shortly after the founding of that city, and that Numa, the immediate successor of Romulus, formed all the workers in this alloy into a kind of community. The author also gives a description of various alloys employed for casting, soldering, brazing, &c., and even mentions the proportions that were used. These alloys were modifications of bronze.

The first account of an alloy of copper and zinc was written by Aristotle; he states that the people who inhabited a country adjoining the Euxine Sea prepared their copper of a beautiful white colour, by mixing and cementing it with an earth found there, and not with tin, as was seemingly the custom. Strabo also alludes to the preparation of an alloy of copper by the Phrygians, from the calcination of certain earths found in the neighbourhood of Andêra; and other authors in the time of Augustus speak distinctly of *cadmia* (*i.e.*, calamine), and its property of converting copper into *aurichalcum*, under which title the zinc alloy was subsequently known.

The brass manufacture was introduced into England in Queen Elizabeth's reign—Daniel Houghsetter and Christopher Schutz, with a body of German workmen, being invited to this country to instruct workmen. A factory was opened in 1565. About a century later Momma and Demetrius opened a brass foundry at Esher, in Surrey, which ultimately failed. These were succeeded by the erection of the celebrated works of the energetic Prince Rupert. From this time the trade grew rapidly: brass cannon were cast at the Temple Water-mill Works at Hackney (still in existence), and foundries were opened at Bristol and Birmingham. The latter town is now the principal seat of the trade in this country. In 1800 Birmingham manufactured about 1000 tons of brass; in 1825 about 10,000 tons; in 1850, 20,000 tons; this rose in 1865 to 38,000 tons, and is at present about 50,000 tons.

Brass may be made by widely differing processes. The mode adopted commercially is to add zinc to melted copper; or to fill a crucible with alternate layers of zinc and copper, the whole being closed in with coke or charcoal. The old method of manufacture was to heat together a finely divided mixture of charcoal, copper, and calamine (native carbonate of zinc) in covered crucibles. Again, copper exposed at a red heat to zinc vapour is converted into brass. The brass wire used in "Lyons gold lace" is made by thus treating copper rods before drawing them out. Copper wire coated with brass may also be prepared by boiling it (after cleaning with nitric acid) in hydrochloric acid and cream of tartar with 1 part of zinc and 12 parts of mercury. Lastly, brass may be produced by electro deposition. (See Electro-Metallurgy.) From a solution of 1 lb. of cupric sulphate and 1 lb. of sulphuric acid in a gallon of water, the electric current deposits a brass which, though solid and compact, has a somewhat botryoidal surface. The addition of 1 oz. of zinc sulphate, according to Napier, renders the deposit tough, compact, and even. From a solution containing a greater proportion of sulphate of zinc the metal is deposited in tufts of needles. Ordinary brassing solutions show the same peculiarity in even a more marked degree, and this makes it impossible to produce a good deposit of more than 0·01 to 0·03 inch in thickness.

H. Walenn has pointed out a reason for this want of cohesion, and also a remedy for it. This form of deposit is, he believes, owing chiefly to a copious evolution of hydrogen taking place during its formation. By employing a solution containing both the oxides and the cyanides of the constituent metals, together with some neutral ammonium tartrate, this evolution of hydrogen may usually be avoided; or should it, nevertheless, take place to a slight extent, it may be entirely stopped by the addition of cupric ammonide. Such a solution yields brass of a uniform character, and the deposit, which may be obtained of any desired thickness, is tough, and has a compact even texture. As there is no evolution of hydrogen, no electric force is wasted, and perfect results may be obtained with a single Wollaston's or Smee's cell.

The whole of the compounds produced by the combination of copper and zinc in different proportions are included in the generic term *brass*. (The old English term was *latten*.) Many of these, however, present great differences in their physical appearance and properties. Alloys of copper and zinc may be made to assume every shade of colour, varying from the whiteness of the latter metal to the deep colour of gold, by a judicious admixture of the constituents. These varieties have been distinguished by fanciful specific names, as Prince Rupert's metal, pinchbeck, Mannheim gold, tutenag, tombac, similor, arcot, potin, &c. In the manufacture of common brass from calamine by the more ancient method, an impure alloy was obtained in the first stages, which is the arcot above mentioned; potin was formed in a similar way, when the finer quality of brass was made; both of these compounds contained a great many impurities.

The following table shows the general character of the principal alloys:—

ALLOYS OF COPPER AND ZINC.—R. MALLET, F.R.S.

| | | Composition per cent. | Spec. gravity. | Colour. | Fracture. | Cohesion per square inch in tons. |
|---|---|---|---|---|---|---|
| 1 | Cu | 100·00 | 8·667 | | | 24·6 |
| 2 | 10 Cu + Zn | 90·70 + 9·30 | 8·605 | Reddish yellow. | Coarse crystalline. | 12·1 |
| 3 | 9 Cu + Zn | 89·80 + 10·20 | 8·607 | Reddish yellow. | Fine crystalline. | 11·5 |
| 4 | 8 Cu + Zn | 88·60 + 11·40 | 8·633 | Reddish yellow. | Fine crystalline. | 12·8 |
| 5 | 7 Cu + Zn | 87·30 + 12·70 | 8·587 | Reddish yellow. | Fine crystalline. | 13·2 |
| 6 | 6 Cu + Zn | 85·40 + 14·60 | 8·591 | Yellowish red. | Fine fibrous. | 14·1 |
| 7 | 5 Cu + Zn | 83·02 + 16·98 | 8·415 | Yellowish red. | Fine crystalline. | 13·7 |
| 8 | 4 Cu + Zn | 79·65 + 20·35 | 8·118 | Yellowish red. | Fine crystalline. | 14·7 |
| 9 | 3 Cu + Zn | 74·58 + 25·42 | 8·397 | Pale yellow. | Fine crystalline. | 13·1 |
| 10 | 2 Cu + Zn | 66·18 + 33·82 | 8·299 | Full yellow. | Fine crystalline. | 12·5 |
| 11 | Cu + Zn | 49·47 + 50·53 | 8·230 | Full yellow. | Coarse crystalline. | 9·2 |
| 12 | Cu + 2 Zn | 32·85 + 67·15 | 8·283 | Deep yellow. | Coarse crystalline. | 19·3 |
| 13 | 8 Cu + 17 Zn | 31·52 + 68·48 | 7·721 | Silver-white. | Conchoidal. | 2·1 |
| 14 | 8 Cu + 18 Zn | 30·30 + 69·70 | 7·836 | Silver-white. | Vitreo-conchoidal. | 2·2 |
| 15 | 8 Cu + 19 Zn | 29·17 + 70·83 | 8 019 | Silver-grey. | Conchoidal. | 0·7 |
| 16 | 8 Cu + 20 Zn | 28·12 + 71·88 | 7·603 | Ash-grey. | Vitreous. | 3·2 |
| 17 | 8 Cu + 21 Zn | 27·10 + 72·90 | 8·058 | Silver-grey. | Conchoidal. | 0·9 |
| 18 | 8 Cu + 22 Zn | 26·24 + 73·76 | 7·882 | Silver-grey. | Conchoidal. | 0·8 |
| 19 | 8 Cu + 23 Zn | 25·39 + 74·61 | 7·443 | Ash-grey. | Fine crystalline. | 5·9 |
| 20 | Cu + 3 Zn | 24·50 + 75·50 | 7·449 | Ash-grey | Fine crystalline. | 3·1 |
| 21 | Cu + 4 Zn | 19 65 + 80·35 | 7·371 | Ash-grey. | Fine crystalline. | 1·9 |
| 22 | Cu + 5 Zn | 16·36 + 83·64 | 6·605 | Very dark grey. | Fine crystalline. | 1·8 |
| 23 | Zn | 100·00 | 6·895 | | | 15·2 |

No. 5 is not quite so good for rolling, hammering, or wire drawing as the common "red brass," which contains less copper in proportion to the zinc. No. 6 very much resembles "red brass," and is quite equal to it in most of its working qualities. No. 7 is well suited for rolling, hammering, and wire drawing; it is known as Bath metal or Prince's metal; the colour now begins to change into brass yellow. No. 8 is German or Dutch brass. No. 9 is brass for rolling. Its working qualities are precisely those of common brass. No. 10 contains 4 per cent more zinc and 4 per cent. less copper than ordinary English brass; it is well suited for rolling, hammering, and wire drawing. No. 11 is a German brass, it cannot be drawn into wire, and cracks under the rollers: is very flexible when strongly heated. It cannot be soldered, as it melts at the same temperature as the solder. No. 12 is a brass used in Germany by watchmakers. It corresponds in composition with "mosaic gold." Nos. 13 to 18 are very brittle; they are too hard to file or turn, but have a lustre when polished which is but little inferior to that of speculum metal. No. 19 breaks under the hammer. Nos. 20 to 22 are very brittle.

Prince Rupert's metal, pinchbeck, and Mannheim gold contain from 75 to 80 per cent., or more, of copper, and on account of their golden colour are employed to some extent in jewellery.

Tombac contains 84·5 per cent. copper and 15·5 per cent. zinc. It is the alloy used for the manufacture of "Dutch metal," an imitation of gold leaf. It can be beaten to a thickness of $\frac{1}{52000}$ of an inch. The tombac is first rolled into sheets and then beat out under a hammer worked by water or steam-power, which gives from 300 to 400 strokes per minute. At first twenty, then forty, and lastly eighty leaves are laid one on the other.

The composition of English brass is about 70 per cent. of copper and 30 per cent. zinc. Lavater found in common brass 70·29 per cent. copper, 29·26 per cent. zinc, 0·17 per cent. tin, 0·28 per cent. lead. Ure puts the composition of fine brass

as 63·5 per cent. copper, 32·3 per cent. zinc; *i.e.*, $Cu_2Zn$.

In the manufacture of brass great care should be taken to free it from iron. This metal does not chemically combine with it at the temperature at which brass is made, and is usually found disseminated in small magnetic particles throughout the mass. Its occurrence happens when an impure calamine is employed in the manufacture, or when old brass containing it is the source of the copper. It renders the alloy prone to rust and tarnish when exposed to the air; making it also hard and dull, and considerably diminishing its tenacity and malleability.

Traces of tin and lead are occasionally detected in various kinds of brass, and sometimes these metals, instead of being injurious, are thought to be somewhat advantageous. Their presence arises from the employment of old brass which had been tinned over or soldered.

Lead is present when rosette copper is employed; its use is mostly confined to the Continental founders. This brass, although it is harder and more brittle than the ordinary kind, is more easily worked under the lathe; it may be welded together, and the junction is not easily broken; in addition, it can be cut with a chisel, sawn, and perforated with facility and exactness. The composition of this variety of brass is, according to Dumas—

| | Unknown. | Stolberg. | Plate Brass of Stolberg. | Plate Brass of Jemmapes. |
|---|---|---|---|---|
| Copper, | 61·6 | 65·8 | 64·8 | 64·6 |
| Zinc, | 35·3 | 31·8 | 32 8 | 33·7 |
| Lead, | 2·9 | 2·2 | 2·0 | 1·5 |
| Tin, | 0·2 | 0·2 | 0·4 | 0·2 |
| | 100·0 | 100·0 | 100·0 | 100·0 |

The proportion of zinc in brass may be varied within certain limits, but when these are exceeded the results are not satisfactory. Practice has fixed the extremes of these between 30 and 38 per cent. of zinc, but as occasion requires the quantity may fall short or exceed this with advantage. Thus, when a rich alloy of considerable tenacity is required, the zinc is reduced to 25 per cent. or less, while with one of little resisting power 50 per cent. of zinc may be used; and should a hard and very brittle compound be desired, the zinc is raised to 60 per cent.

The alloy used as gilding metal should be easily melted and flow freely, should admit of being engraved and turned with facility, and of being gilt with the smallest possible quantity of gold. It will possess the latter quality if the grain of the brass is very fine and compact. All the alloys which are devoted to these uses are not, however, homogeneous in their composition, as the appended analyses of a few of them show—

| | 1. | 2. | 3. | 4. | 5. |
|---|---|---|---|---|---|
| Copper, | 63·70 | 64·45 | 78·48 | 78·84 | 82·3 |
| Zinc, | 33·55 | 32·44 | 17·22 | 17·31 | 17 5 |
| Tin, | 2·50 | 0·25 | 2·87 | 0·96 | 0·2 |
| Lead, | 0·25 | 2·86 | 1·43 | 2·89 | 0·0 |
| | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

The densities of the first and second alloy here mentioned are respectively 8·395 and 8·542. These are the best adapted for the purposes of the jeweller. In the other three samples the amount of copper is much larger, although intended for the same purpose, and very often it is increased to 90 and 95 per cent., in which case it is analogous to chrysocolla. The product is then called gilding metal, while the others are termed Bath metal, pinchbeck, Mannheim gold, and "similor." Lead and tin do not affect the quality of the brass for certain works; but where it is requisite that the brass should be very tenacious the least quantity of these metals will prove detrimental. Thus appreciable amounts of lead or tin are highly injurious in brass of which it is intended to make wire; nevertheless this kind of alloy always contains traces of other metals, as the following analyses of wire-brass show:—

| | Per Cent. | Per Cent. |
|---|---|---|
| Copper, | 66·2 | 67·0 |
| Zinc, | 33·0 | 32·0 |
| Tin, | 0·8 | — |
| Lead, | | 0·5 |
| Antimony, | — | 0 5 |
| | 100·0 | 100·0 |

Another variety of brass, which is employed in operations where it is requisite that the metal should work well under the hammer, is composed of copper and zinc in the following proportions:—

| | |
|---|---|
| Copper, | 70·1 |
| Zinc, | 29·9 |
| | 100·0 |

Metal for the manufacture of pieces of machinery and locomotives has the composition—

| | |
|---|---|
| Copper, | 74·5 |
| Zinc, | 25·0 |
| Lead, | 0·5 |
| | 100·0 |

The fracture of this alloy is of a fine yellow colour; it is not so malleable as those in which the quantity of zinc is less. Generally, as the percentage of zinc increases the malleability is decreased; hence, for working brass, the best varieties are obtained when the zinc constitutes from 20 to 33 per cent. of the whole.

Brass Manufacture.—Brass founders in place of percentage composition speak of the amount of zinc only, it being understood that the ratio is to the pound of copper. Thus they would say to make copper cast well alloy one-eight to half an ounce of zinc with each pound of metal. The manner in which this is sometimes done is by fusing four ounces or less of brass with the above quantity of metal. The proportion reckoned upon in making "gilding metal" is one to one ounce and a quarter of zinc; and, like the foregoing, this alloy is not made by the union of its components directly, but by the fusion of a definite proportion of brass and copper. In red sheet brass the pound of copper is proportioned to three ounces of the secondary metal.

Mannheim gold, pinchbeck, Bath metal, and several other alloys, all of which possess more or less of a

golden colour, are formed with three or four ounces of zinc to the pound. The true brass, from which all the other varieties are called, is formed of two parts of copper and one part of zinc; and metal which bears soldering well, such as Bristol brass, contains a smaller quantity of the secondary metal.

The following table exhibits the proportion in which these are employed, namely:—

| | Bristol brass. | Muntz metal. | Muntz sheathing. | Spelter solder. | Pale yellow metal. | Mosaic gold. |
|---|---|---|---|---|---|---|
| | oz. | oz. | oz. | oz. | oz. | oz |
| Copper,.. | 16 | 16 | 16 | 16 | 16 | 16 |
| Zinc,.... | 6 | $10\frac{2}{3}$ | 9 to 16 | 12 to 16 | 12 | $16\frac{1}{2}$ to 17 |

It is always necessary to employ somewhat more zinc than is here mentioned, in order to cover the quantity which is volatilized by the great heat usually resulting from the union of the two metals; unless this precaution be taken, or provision be made for preventing the volatilization of the zinc, the resulting alloy will often be quite different from what was intended.

Long before the isolation of zinc, and when, consequently, its combination with copper could not be effected directly as is now generally done in brass-foundries, the ancients were well acquainted with brass and the method of preparing it. The course they followed, and which was in practice in this country thirty years back, was to fuse the copper with an ore of zinc and charcoal, by which treatment the zinc was reduced and combined with the copper without becoming known as a distinct body. Calamine, blende, and other compounds of zinc were commonly used in the manufacture, but it was customary for these to undergo a calcination before they were fused with the copper and charcoal. This method has now so completely died out that it is doubtful if a single calamine furnace remains in England.

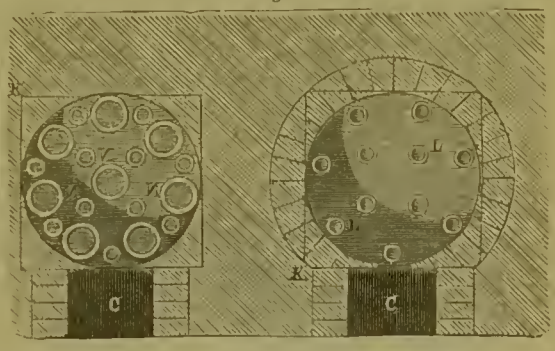
The materials which the founder employed in manufacturing brass in this way were bean copper or rosettes (from which the silver had been abstracted by eliquation with lead), calcined calamine, blende, and charcoal, the proportion of the latter two being regulated according as it was intended to produce red or yellow copper.

In this method it was of great importance that the zinc ore should be free from any sulphurous compounds, and also from silicate of zinc; the former was injurious, inasmuch as it rendered the alloy brittle and of a bad colour, and the latter was not reduced in the crucible in the ordinary way, although, by the aid of lime or carbonate of lime, it might be made to yield its zinc to the copper, while the silica flowed off in combination with the earthy base. Another matter of importance was, that the material should be well calcined, otherwise the reduction of the zinc would be more difficult than if roasting was properly executed. Frequently this operation was performed by placing alternate layers of calamine and coal or charcoal upon one another in the form of a mound, the base being formed of large billets of wood. The mass was ignited at the top.

After calcination the roasted mineral was prepared for the operation of smelting and uniting it with the copper, by grinding it under head-stones, and subsequently sifting to remove the grosser particles. With rosette, grain, or bean shot copper the alloy thus made was seldom richer in zinc than 27 or 28 per cent.; and before it was fit for the market it had to be melted with a fresh quantity of the ore in order to bring it to the marketable standard. Sometimes old brass and other cupreous matters were used in founding the metal in this way; in such cases impurities in the shape of lead, iron, tin, were incorporated. This has to be borne in mind in analyzing old brasses.

Two distinct operations were followed in preparing the brass by this method; the first, to form the alloy just mentioned, generally known as *arcot*, and the second, to render this marketable by combining it with a further proportion of zinc. The fusion was

Fig. 1.



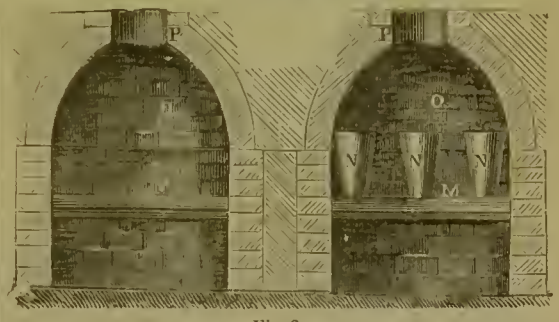




Fig 2.

effected in large crucibles or pots, placed in a circular hearth, as in the case of bismuth.

Figs. 1 and 2 represent the furnaces used in the brass foundry, Fig. 1 being a plan and Fig. 2 a section of the oven. K K are square cast plates which form the base of the oven. These plates are perforated in eleven places, as seen at L L, for the purpose of carrying air into the kiln, and allowing the cinders and ashes from the fuel to fall into the pit beneath. M M, the area or floor of kiln, made of refractory clay. N N are the pots for fusing the material, of which eight are in each kiln; and O O, the arches over them, which are cast in moulds, and are composed of the same material as that of which the pots are made, only less care is bestowed upon them than upon the latter. When finished the mould, which consisted of seven or eight parts, was sundered. The arch was some inches flat at the base, that it might press

strongly and securely. P P P represent the top casting, which forms the mouth of the kiln, opening into the cover, which rests upon the arch.

The height of the kilns was equal to their breadth, which was about 1½ foot. They were each capable of holding six or eight pots, the capacity of which was such as to contain collectively from 1 to 1½ cwt. of brass. The fuel employed was generally coke or coal in pieces of moderate size, so as not to intercept the draught. The furnace and pots being heated, the attendant took one of the latter and filled it to the brim with the mixture of calamine and charcoal, and then forced into it the necessary quantity of the rosette or grain copper, or arcot, by a few blows of a mallet or hammer, and after this was done, sprinkled a few handfuls of the charcoal mixture on the surface. The crucible was then deposited in the fire, and others charged in the same way in succession, till the kiln was full. Pieces of fuel were then added in such quantities and in such a manner that the pots were covered, but not overloaded with them. The furnace was then closed and left undisturbed for six or seven hours, the temperature being kept up for the whole time. At the end of this period the contents of the pots were at a white heat: the fire was again revived and kept in active combustion for a short time, until the fumes of the volatilizing zinc, which are significant of the reduction and fusion of the metal, appeared. As soon as this happened the fire was checked, in order that the copper might not melt too rapidly, and thus prevent the prolonged exposure to the fumes of the melted zinc, which exposure is essential to insure a good combination. About three or four hours served to effect this process. When the combination was complete, the pots were removed from the kiln, and the dross or portion of oxide on the surface skimmed off and the casting made.

At Holywell, in North Wales, the calamine was found mixed with a large quantity of lead ore, which was removed by picking, grinding, and washing. The calcination was then performed in the ordinary way, and with the usual precautions of stirring, &c., in a furnace the bed of which was almost horizontal. After the roasting the material was reduced to powder in a mill, and at the same time mixed with about one-fourth of its weight of charcoal. The crucibles or pots, made of refractory clay, were filled with this mixture, and the proper amount of red or grain copper, and the covers luted on with a material composed of refractory clay and horse dung. The proportion of the materials was for the most part—

40 lbs. of grain copper, and
60 " of calamine and charcoal mixture;

from which 60 lbs. of brass, containing 33 per cent. of zinc, was obtained. The period of reduction and combination was about twenty-four hours.

In fusing the mixtures above described no scoriæ are produced, all the silica being united with substances which do not enter into fusion at the temperature of the kiln or pot. Hence the great loss which resulted from the use of zinc compounds which contain much zinc silicate, for besides what was liable to be lost by the oxidation of some of the reduced metal, all this passed away unchanged.

The manufacture of brass from calamine was exceedingly laborious, and the expenditure in fuel was such that more than twice the quantity was used than is requisite now that the alloy is made by fusing the metals together. Another advantage in the latter mode is that more than double as much as could be procured by the old method can be formed in twenty-four hours with far less labour. The principal difficulty to be contended with in the present mode of working is the rapidity with which the zinc is deprived of its property of alloying with the metal, owing to its affinity for oxygen. For this reason, when the proportions of an alloy as determined by chemical analysis are synthetically employed to form a similar article, the result is generally a failure; either more of the metal prone to oxidize must be employed, so as by this excess to make up for that which becomes lost, or some means must be adopted to exclude the "foul" air, as it is termed in the language of the workman. Covering the alloy with suitable fluxes renders great service in this respect, not only in preventing the oxidation, but, as a consequence of the first, excluding this oxide from afterwards mixing with the metal and injuring its quality. Salt cake is commonly used for this purpose. The loss of zinc would be much greater were it not for the strong affinity which exists between it and copper. This has been taken advantage of in a process for coating copper with brass, in which sheet copper at a high temperature is simply exposed to fumes of zinc.

The late Earl of Rosse recommended a furnace or kiln deeper than usual, and the covering of the metal at all times with a layer of powdered charcoal 2 inches thick. When these conditions are fulfilled it is affirmed that only about the 180th part of the zinc is lost. Holtzapffel found that under ordinary circumstances the loss is at the least a thirtieth of the whole alloy. He fused 24 lbs. of copper, and determined the loss which was thus sustained. An equal weight of the same material was afterwards fused; 12 lbs. of zinc in plates of about three-fourths of an inch thick were then broken up into convenient-sized fragments, which were added one by one at regular intervals to the fused copper till the whole was introduced. When this happened the surface of the liquid compound metal was covered with glass and left to the action of the heat for fifteen minutes, or till such time as the fumes of zinc gave indications that the contents of the pot were in perfect fusion. Having removed the pot from the fire, stirred its contents for a short time, it was cast, and the result of two experiments thus conducted showed that instead of obtaining 33⅓ per cent. of zinc, the proportion found was 31¼, or 7¼ ounces of zinc instead of 8 to the pound. Further, on remelting quantities of this alloy it continued to lose zinc, till after the sixth operation the alloyed metal was reduced to 4⅝ ozs. to the pound.

The direct preparation of brass by the combination of the two metals is in ordinary brass foundries brought about by fusing first the copper and then the zinc in crucibles, or (a much more wasteful mode of working) in reverberatory furnaces.

The crucibles employed are either of burned fire-clay, Hessian, Berlin, or Stourbridge, or of a mixture of 1 part of fireclay with 2 parts of blacklead. These latter, termed blue pots, are then carefully dried in a kiln. They are found to stand sudden changes of temperature without cracking, and are non-porous at the highest degree of heat they are likely to be subjected to: hence they have almost entirely superseded the burnt fireclay crucibles.

In the early days of brass founding the zinc was melted first, and pieces of copper gradually added, the heat of the furnace being raised by degrees as the fusing point of the alloy became higher.

The modern method of working reverses the proceeding; the copper is melted first, and the zinc, first having been made hot, is added by small instalments until the fusion is complete.

After the furnace is well alight, the crucibles are placed on the hearth bottom upwards and heated to redness; they are then set the right way, and the charge of copper introduced, to prevent oxidation a few pieces of charcoal being placed in the mouth of each crucible. The heat of the furnace is then gradually raised until the whole of the copper is fused. The zinc in small pieces has been in the meantime getting hot at the mouth of the furnace; it is now seized piece by piece with crucible tongs and held beneath the surface of the melted copper until dissolved. When the whole of the charge is in the crucibles and fused, it is well stirred with a hot brass or iron stirrer, and then decanted into the moulds or into a casting vessel, if the contents of several crucibles are required for a large casting. The fuel should be good coke.

The English furnaces are either square or round. The square furnace is built up exclusively of cast-iron plates, bolted together by strong tie-rods; within this iron casing 18-inch brickwork forms a chamber to hold a single crucible. The round furnace is a cast or wrought-iron cylinder, 2 feet in diameter by 4 feet long, lined with fire-clay, so that its internal width is reduced to about 1 foot. The bottom of each furnace is formed of ordinary furnace bars, the air being admitted, as in the foreign furnaces, through a sunken ash-pit which communicates with the outside of the building. The mouth of the furnace is closed by a loose cast-iron cover, which can be luted down.

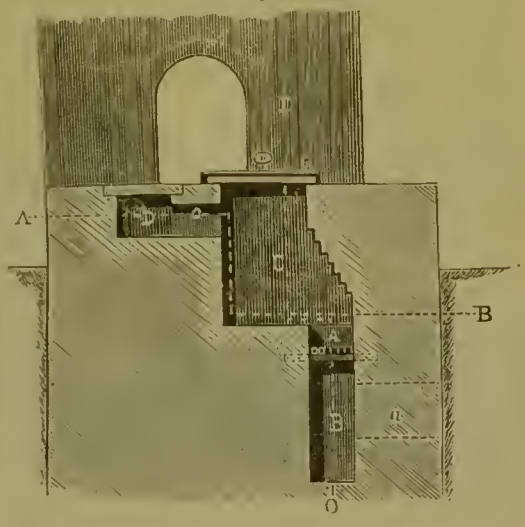
A form of brass furnace in use in Germany, to be heated with coal, has an oval chamber with a flattened ceiling. The sole of the furnace is within this chamber, and communicates with it by ray-like disposed through its walls.

The furnace bottom with its connecting walls thus forms a star-shaped chamber with an opening in the middle, from which the ray-like channels proceed to the periphery. The crucibles, of any desired circumference, stand upon this hearth, and beneath it is the fire grate for the coal, the flame from which traverses first the oval chamber and then through the numerous openings the hearth itself. The crucibles are introduced through an opening in the crown of the furnace, which is afterwards closed by a well fitting iron plate provided with a handle, by which it can be lifted up when desired.

Blast furnaces are likewise used, some of which hold one, others two crucibles. The crucibles stand either on the fire grate itself, or upon a flat hearth just above the arch of the fire grate.

Figs. 3 and 4 show an oven with a separate fire, much used in Belgium. A is the fire grate, B the ash-pit. This has a wide canal, *a*, cut through it for the admission of air to the fire. C is the melting chamber; it will be observed that the hearth is raised somewhat above the level of the fire bars. The flues, *c*, lead into the chamber D, which is furnished with a damper at *d* for the regulation of

Fig. 3.




the draught. The products of combustion are finally carried off by the flue, E, into the chimney shaft. A portable iron cover, *e*, is over the opening; through which first the crucibles, and afterwards the copper and zinc, are put into the furnace.

In large foundries the melting ovens are now very generally heated by Siemens' regenerative furnace. (See Fuel.)

When it is desired to cast brass into ingots, moulds are employed which are sometimes made of blocks of granite bound together with iron, and having the intervening space regulated by bars of iron, the thickness of which corresponds to the intended casting. Usually, however, the moulds are of cast iron. They must be heated before the molten brass is poured into them.

Previous to tapping the furnace, samples are taken out, cast into ingots, and passed through the rolls whilst still hot, and afterwards broken across. The fracture which presents itself should be close and have a very fine grain; if the testing is unsatisfactory more and more zinc is added, until the test ingot shows the desired quality.

Brass subject to tension sometimes undergoes a remarkable molecular change; loses its tenacity, and in a short time becomes almost as brittle as glass. The circumstances under which this change takes place have never been investigated.

Brass which contains more than 50 per cent. of copper behaves like copper in the voltaic cell, and does not precipitate the salts of copper; while that which has an excess of zinc decomposes copper salts and becomes converted into pure copper: it dissolves completely in acids which do not attack copper alone.

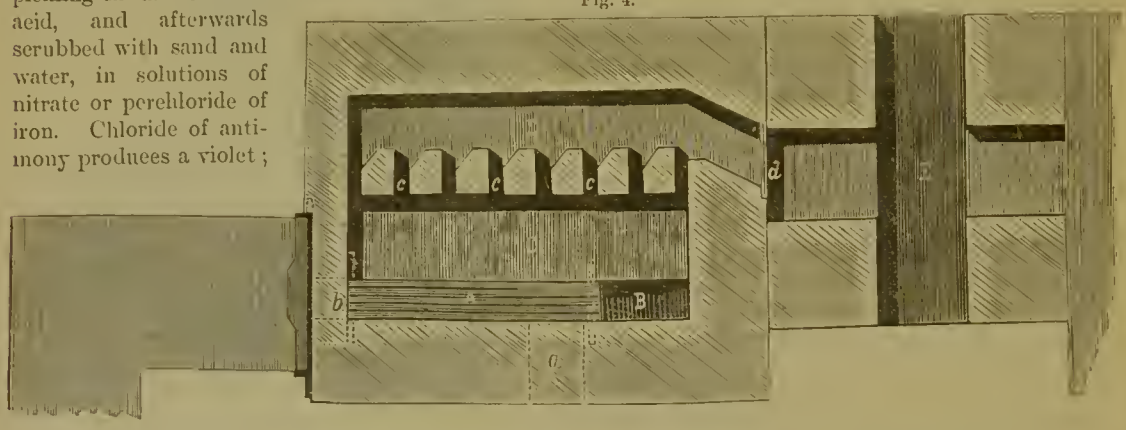
Brass expands $\frac{1}{533}$th of its length on being heated, and when hot can be rolled or beaten to any required thinness.

Bronzing.—To prevent continuous oxidation of brass it is the custom to induce a surface oxidation, which shall form a protecting coating over the rest of the metal. Various shades of colour are obtained by varying the oxidizing agents and the degree of oxidation. Brass left in wet sand becomes brown, but this colour is given much more expeditiously by dipping brass which has been well cleansed by pickling in dilute nitric acid, and afterwards scrubbed with sand and water, in solutions of nitrate or perchloride of iron. Chloride of antimony produces a violet; arsenious acid grey (by the deposition of a film of the metal); black is obtained with bichloride of platinum; green by dipping in a solution of iron and arsenic in muriatic acid. Almost any colour may be obtained by making a mixture of 2 oz. of pernitrate of iron and 2 oz. of hyposulphite of soda in 1 pint of water, and immersing the brass in the liquor until the required shade makes its appearance, then wash well with water, dry and brush. One part of perchloride of iron to 2 parts of water mixed together, and the brass immersed in the liquid, gives a pale or deep olive green, according to the time of immersion. If nitric acid is saturated with copper, and the brass dipped in the liquid and heated, it assumes a dark green.

*Black Bronze for philosophical instruments.*—Dip the brass in aquafortis, rinse the acid off with clean water, and place it in the following mixture until it turns black:—Hydrochloric acid, 12 lbs.; sulphate of iron, 1 lb.; pure white arsenic, 1 lb. It is then taken out, rinsed in water, dried in sawdust, polished with blacklead, and coated with green lacquer.

Lacquering.—The brass is made as clean and

Fig. 4.




bright as possible, either by polishing or pickling: in the latter case it is dried in hot sawdust. After which, for dead brass, it is dipped for an instant in a solution of 1 part of nitric acid with 4 of water; if bright brass is desired, it is dipped in strong commercial nitric acid; and in any case it is finally, to preserve the colour until lacquered, well washed in water containing argol.

The articles to be lacquered are heated on a hot plate, and varnished with one of the following lacquers:—

*Pale Lacquer.*—1 gallon of methylated spirit, 5 oz. of shellac, 4 oz. of gum sandarach, and 1 oz. of gum elemi; mix in a tin flask, and expose to a gentle heat for a day or two, then strain off and add half a gallon of spirit to the sediment and heat as before.

*Green Lacquer.*—Add to the pale lacquer, when mixing, 6 oz. of turmeric and 1 oz. of gum gamboge.

*High-coloured Lacquer.*—2 quarts of methylated spirits, 2½ oz. of shellac, 2 oz. gum sandarach, ½ oz. gum elemi; mix and keep gently warmed for two or three days; strain colour with dragon's blood to taste, and thin with 1 quart spirits of wine.

*Common Lacquer.*—1. Seed-lac, dragon's blood, gamboge, of each 4 oz.; saffron, 1 oz.; spirits of wine, 10 pints. 2. Shellac in spirits of wine in the proportion of 1 oz. to the pint. Colour with red sanders, dragon's blood, or annotto, for red-tinged lacquers, or with turmeric, saffron, sandarach, or gamboge, for yellow lacquers.

The brass must not be heated beyond the boiling point of the varnish, and after lacquering must be returned to the hot plate until the lacquer has set.

Muntz's Metal.—This kind of brass is generally composed of 40 parts of zinc with 60 of copper. The metal after being properly melted is cast into ingots, heated to a red heat, and rolled into sheets. The sheets are pickled with dilute sulphuric acid to free them from adhering scale, and afterwards washed in water. It is of importance that the heat be maintained at nearly a red heat during the rolling, as otherwise the metal frays and cracks. In 1846 a patent was taken out by Muntz for an alloy, which consists of 56 per cent. of copper, 43·25 zinc, and 0·75 lead. The alloy is cast into ingots, which are to be rolled at a red heat.

MUNTZ'S metal, or "Patent Yellow-metal Sheathing," as it is called, has almost entirely superseded copper sheathing for merchant-ships. It is said that by the exposure to sea water of this brass the zinc slowly and uniformly corrodes over the entire surface, and while so doing prevents barnacles, &c., from attaching themselves. "FARADAY," says Dr. PERCY, "informed me, that in a specimen of sheathing formed of the alloy in question, which had been long exposed to the action of sea water, he found no zinc remaining."

MUNTZ'S metal is almost always cast in reverberatory furnaces, the zinc being added to the melted copper; when the fusion is complete the furnace is tapped, and the alloy runs off into a fire-clay receptacle, from whence it is ladled into iron ingot moulds of a suitable size for the rolling-mill. These moulds must be oiled and lightly dusted with charcoal.

GERMAN SILVER.—*British plate; cuivre blanc, maillechort*, French; *argentan, neusilber, weisskupfer*, German.—This is an alloy of nickel, copper, and zinc, which owes its peculiarity more to the first than to the other metals; still, as the copper is the main ingredient, a brief account of it will be given here as one of the copper alloys. It has long been known to the Chinese under the name *pakfong*, or white metal. It was first introduced into this country from Germany, as its name implies, where it had been prepared by smelting an ore found at Hilburghausen, near Suhl, in Henneberg. KEFERSTEIN found this alloy contained—

| | Per Cent. |
|---|---|
| Copper, | 40·4 |
| Nickel, | 31·6 |
| Zinc, | 25·4 |
| Tin, | 2·6 |
| | 100 0 |

The Chinese pakfong always contains 2 or 3 per cent. of iron, and this is said to give it a brighter colour, and to render the alloy more compact; but then it confers hardness and brittleness also, and these militate against its use in many cases. As the nickel necessary to prepare German silver is much rarer than the other constituents, metallurgists have considerably diminished its proportion, substituting zinc; in doing so the brightness of the alloy is not much impaired, so long as the ratio remains within a certain limit, but once this is passed the compound presents a fair appearance for a very short time, and then assumes the hue of pale brass. The following table represents the composition of a number of these alloys:—

| | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. | 11. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Copper, | 43·8 | 40·4 | 53·4 | 50·0 | 65·4 | 60·0 | 57·0 | 59·2 | 55·0 | 51·6 | 45·7 |
| Nickel, | 15·6 | 31·6 | 17·5 | 18·7 | 16·8 | 20·0 | 20·0 | 14·8 | 20·6 | 25·8 | 34·3 |
| Zinc, | 40·6 | 25·4 | 29·1 | 31·3 | 13·4 | 20·0 | 20·0 | 26·0 | 24·4 | 22·6 | 20·0 |
| Iron, | — | 2·6 | — | — | 3·4 | — | Lead, 3·0 | — | — | — | — |
| | 100·0 | 100 0 | 100·0 | 100·0 | 100 0 | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 | 100·0 |

Numbers 1 and 2 are the analyses of samples of Chinese pakfong, the latter being a very superior quality in point of colour and structure, so that it can be very highly polished. 3 and 4 represent the composition of alloys prepared by FRICK. They resemble very much a silver alloy containing about 18 carats to the ounce. They are hard, but very tough and ductile, becoming soft by immersing into cold water, and their specific gravity at 67° Fahr. is 8·556. Number 5 is *maillechort* made at Paris, having a specific gravity of 7·18. It may be rolled out into very thin plates and polished to a high degree. It loses about 12 per cent. when heated, and this loss renders it much whiter than before. Numbers 6 and 7 are recommended by GERSDORFF of Vienna, the first for forks and such like articles, and the second for such objects as require soldering. The commonest German silver is, according to TOPPING, represented by number 8. It should be used only for wire-drawing and other common purposes. If the quantity of nickel be reduced below this, the alloy will be little better than pale brass, and will tarnish rapidly. Number 9 is a very beautiful compound, but little inferior in appearance to standard silver. It is often preferred to the more costly compounds. The richest alloy which can be made, without injuring the mechanical properties of the metal, is number 11. It is a very beautiful compound, but more difficultly prepared than the preceding, owing to its requiring a high temperature for its fusion.

An alloy called *tutenag*, and composed of 45·7 of copper, 17·4 of nickel, and 36·9 of zinc, is very serviceable, especially for casting. It is in frequent use among the Chinese. It is very fusible, but hard, and not easily rolled, and in colour resembles very much the alloy *electrum*, the analysis of which is given in number 9 of the foregoing table.

Much nickel silver is manufactured at Sheffield; the proportions of the ingredients are as follows:—

| | Common. | White. | Electrum. | Infusible. | Tutenag. |
|---|---|---|---|---|---|
| Copper, | 8 | 8 | 8 | 8 | 8 |
| Zinc, | 3·5 | 3·5 | 3·5 | 3·5 | 6·5 |
| Nickel, | 2 | 2 | 4 | 6 | 3 |

H. WATTS gives the composition of nickel silver for spoons and forks as:—2 parts copper, 1 nickel, 1 zinc; for knife and fork handles:—5 parts copper, 2 nickel, 2 zinc. The addition of 3 per cent. of lead to the first of these mixtures, or 2 per cent. to the second, yields an alloy adapted for casting.

A small quantity of iron hardens considerably these alloys, and likewise gives a bright colour; but it renders the metal more difficult to work.

German silver is prepared by melting together the constituents of the alloy; the work is performed in pots or crucibles in the same way as in the manufacture of brass, and much of the zinc passes off by volatilization and oxidation. By care, however, this loss may be reduced to some extent; still a large quantity escapes, which must be made up in the alloy by taking a larger proportion of zinc. It is the usual custom to have the metals arranged in

alternate layers in the crucible, the lowermost and topmost being copper; charcoal powder, dust, or powdered glass are strewn upon the surface. Or it may be made by melting the metals consecutively: in this case the copper is fused first, then the nickel is added, and when the whole is melted the zinc put into the crucible piece by piece, and held beneath the surface until absorbed. When the metals enter into fusion, it is necessary that the contents of the pot should be stirred with a porcelain rod, in order that the compound may be homogeneous.

Nickel silver has a crystalline structure when solidified from fusion. It must therefore be heated to dull redness and cooled again completely before it is rolled or hammered, but when once the crystalline structure has been destroyed the alloy may be worked like brass.

Chinese nickel silver may be heated to dull redness without losing its malleability, but if the temperature is carried beyond this point it flies to pieces with a very slight blow.

BRONZE.—This alloy is composed of copper and tin; it is the compound which was known to the ancients under the name of *brass*, and of which they made all their implements of war and domestic economy before iron came into general use.

The principal uses of bronze are in the making of the baser currency, in statuary, cannon and bell founding, in casting medals, &c. The rage for statues of this metal was very great in the time of Alexander the Great. Castings in bronze had long before been made; but the celebrated artist Lysippus, by his discovery of the means of moulding, afforded such facilities for the art that so many bronze statues were erected that Pliny called them the *mob of Alexander*. Huge colossi were also raised and multiplied, and it is related that Mutianus, the Roman consul, found 3000 bronze statues at Athens, the same number at Rhodes, and as many at Olympia and Delphi.

Mallet gives the characteristics of various alloys of copper and tin in the following table:—

| Copper. | Specific Gravity. | Colour. | Fracture. | Tenacity. | Order of Malleability. | Order of Hardness. | Order of Fusibility. |
|---|---|---|---|---|---|---|---|
| Per Cent. | | | | | | | |
| 100 | 8·607 | .. | .. | 24·6 | 1 | 10 | 16 |
| 84·29 | 8·561 | Reddish yellow. | Fine grain,..... | 16·1 | 2 | 8 | 15 |
| 82·81 | 8·462 | " | " ..... | 15·3 | 3 | 5 | 14 |
| 81·10 | 8·459 | " | " ..... | 17·7 | 4 | 4 | 13 |
| 78·97 | 8·728 | " | Vitreous conchoidal, | 13·6 | 5 | 3 | 12 |
| 76·29 | 8·750 | Pale red, ..... | " | 9·7 | Brittle,.. | 2 | 11 |
| 72·80 | 8·575 | " ..... | " | 4·9 | " .. | 1 | 10 |
| 68·21 | 8·400 | Ash grey,..... | " | 0·7 | Friable,. | 6 | 9 |
| 61·69 | 8·539 | Dark grey,.... | Laminar,..... | 0·5 | " . | 7 | 8 |
| 51·75 | 8·416 | Greyish white,. | Vitreous conchoidal, | 1·7 | Brittle,.. | 9 | 7 |
| 34·92 | 8·056 | Whiter,..... | Laminar,..... | 1·4 | " .. | 11 | 6 |
| 21·15 | 7·387 | | Vitreous,..... ..... | 3·9 | " .. | 12 | 5 |
| 15·17 | 7·447 | Still whiter,.... | " .. ..... | 3·1 | 8 Tough, | 13 | 4 |
| 11·82 | 7·472 | | Laminar,..... | 3·0 | 6 " | 14 | 3 |
| 9·68 | 7·442 | | Earthy,..... | 2·5 | 7 | 15 | 2 |

Bronze is more fusible than copper. Its density is greater than the mean of its constituents; but this is subject to some little derangement, owing to the vesicular structure which the ingot or casting assumes at the point of solidification, by which its bulk is increased, and of course the real gravity of the metal reduced. Hence, to ascertain the true specific gravity of bronze, portions of the ingot should be cut off and reduced to fine powder, and weighed in this state; and the extent of the preceding error might be determined by ascertaining the apparent density in the bulk previous to the reduction to powder, and comparing it with the secondary results. The following table of a few of these alloys shows their calculated specific gravity, and the difference between these and the mean as found in practical working:—

| Alloy. Copper. | Tin. | Observed density. | Calculated density. | Difference. |
|---|---|---|---|---|
| 96·2 .... | 3·8 .... | 8·79 .... | 8·74 .... | 0·05 |
| 94·4 .... | 5·6 ..... | 8·78 .... | 8·71 .... | 0·07 |
| 92·6 .... | 7·4 .... | 8·76 .... | 8·68 .... | 0·08 |
| 91·0 .... | 9·0 .... | 8·76 .... | 8·66 .... | 0·10 |
| 89·3 .... | 10·7 .... | 8·80 .... | 8·63 .... | 0·17 |
| 87·7 .... | 12·3 .... | 8·81 .... | 8·61 .... | 0·20 |
| 86·2 .... | 13·8 ... | 8·87 .... | 8·60 .... | 0·27 |
| 75·0 .... | 25·0 .... | 8·83 .... | 8·43 .... | 0·40 |
| 50·0 .... | 50·0 .... | 8·79 .... | 8·05 .... | 0·74 |

The alloys in most general use are bell-metal, composed of about 78 parts of copper to 22 of tin; gun metal, which consists of 90 parts of copper and 10 of tin; and statuary bronze, which commonly contains lead and zinc as well as tin.

A peculiar behaviour of bronze when cast in sand moulds, more especially if they be large, is that shortly after casting a jet of liquid metal issues from the interior, either at the sides or at the upper surface of the metal. This has been accounted for by supposing that the first portion of the alloy which comes in contact with the walls of the mould condenses, and in so doing contracts to some extent, and by this means displaces the more expanded molten matter inside; and if the pressure of the metal from above is considerable, so as to prevent the ascent, it will exude laterally; but when the weight thus bearing upon it is not very great, it forms an upward current. It has been found that the metal thus thrown out is much richer in tin than the remainder of the alloy, and that in these parts also great variations are often detected, as the annexed table, from the experiments of Dussaussoi, who examined two castings with the following results:—

| | | At the surface, and within six inches of the base. | At the centre, and within six inches of the base. | At the top surface. |
|---|---|---|---|---|
| Ingot 3 inches square, and 13 in height, weighing 40 lbs., | Copper, | 89·09 | 90·63 | 90·54 |
| | Tin, | 11·91 | 9·46 | 9·46 |
| | | 100·00 | 100·00 | 100·00 |
| An ingot of the same dimensions moulded in sand, | Copper, | 90·0 | 90·9 | 83·6 |
| | Tin, | 10·0 | 9·1 | 16·4 |
| | | 100·0 | 100·0 | 100·0 |

Bronze containing about 85 per cent. of copper and the remainder of tin is somewhat malleable. This property can be communicated to a much greater extent by tempering the metal like steel, but with opposite effects. Even alloys composed of proportions different from the foregoing may, by a similar treatment, be made to work under the hammer. The tempering in this case lessens the density of the metal, as also the hardness; it affects the malleability and flexibility, and sometimes renders it more tenacious, besides giving a duller tone to the sound of the alloy.

Many articles require in their preparation that the bronze should partake of some of these properties, and therefore objects after being cast are often slightly tempered, that they may be made more easy to work under the hammer, the lathe, or the press, and when thus finished the hardness is recommunicated by heating them.

According to Dussaussoi, the alloy which best comports itself under this treatment is composed of 8 equivalents of copper and 1 of tin. Bronze of this composition, he states, always increases in tenacity when the ingots or objects are of some thickness, whereas, with the most part of the others, the contrary is the case. The annexed table shows the results of some experiments which he made upon his subject:—

| | Composition of the alloy, centesimally. | | | | |
|---|---|---|---|---|---|
| Copper, | 95 | 90 | 85 | 80 | 75 |
| Tin, | 5 | 10 | 15 | 20 | 25 |
| | 100 | 100 | 100 | 100 | 100 |
| Density before tempering, | 7·92 | 8·08 | 8·46 | 8·67 | 8·57 |
| Density after tempering, | 7 89 | 8·00 | 8·35 | 8·52 | 8·31 |
| Hardness before tempering, | 100 | 100 | 100 | 100 | 100 |
| Hardness after tempering, | 99 | 98 | 96 | 92 | 91 |
| Sample ¾ths of a line in thickness, before tempering, tenacity, | 80 | 66 | 48 | 50 | 70 |
| Sample ¾ths of a line in thickness, after tempering, tenacity, | 100 | 100 | 100 | 100 | 100 |
| Sample of eight lines in thickness, before tempering, tenacity, | 100 | 100 | 80 | 80 | 100 |
| Sample of eight lines in thickness, after tempering, tenacity, | 75 | 78 | 100 | 100 | 35 |

Other circumstances tend to modify the quality of bronze considerably, the principal of which is the liability to alter in composition during the melting, by the oxidation of the tin. Many large castings manifest this imperfection to a considerable extent, more especially if the metal required many fusions before the objects were finished. That of Desaix in the Place Dauphiné, and the column in the Place Vendome, are noted specimens of most defective workmanship, owing to the want of knowledge in regard to the cause of the defect already mentioned.

On analyzing, separately, specimens taken from the bas-reliefs of the pedestal of the latter column, from the shaft and from the capital, it was found that the first contained, centesimally, 6 of tin and 94 of copper, the second contained much less tin than the first, and in the third, the tin was found as low as 0·21. Hence it will be seen that the founder, instead of maintaining the alloy at its average composition, allowed the copper to be gradually refined, the other metal being thrown off as oxide. If the alloy be exposed to the air during the fusion, both the metals constituting it will be oxidized, but in very unequal proportions; thus, in an alloy composed of 91 parts of copper and 9 of tin, for every part of the latter which is thrown off, there are two or three of the former, but it is evident that ultimately the mass would be deprived of all the tin. The numbers annexed show the extent of the oxidation, and the variation in gravity which took place in the sample studied. The alloy was ordnance metal, cast in sand, and contained 90 parts of copper and 10 of tin.

| Number of fusions. | Weight of ingot in ounces. | Loss per cent. | Specific gravity. | Composition. Copper. | Composition. Tin. |
|---|---|---|---|---|---|
| 1 | 268 | 1·2 | 8·565 | 90·4 | 9·6 |
| 2 | 236 | 1·6 | 8·460 | 90·7 | 9·3 |
| 3 | 204 | 2·1 | 8·386 | 91·7 | 8·3 |
| 4 | 172 | 2·5 | 8·478 | 92·8 | 7·2 |
| 5 | 140 | 2·6 | 8·529 | 93·7 | 6·3 |
| 6 | 104 | 3·0 | 8·500 | 95·0 | 5·0 |

In addition to the loss suffered by the oxidation, another of a more serious nature attends it, namely, the incorporation of some protoxide of the metals in the alloy, which renders it brittle, and not calculated to wear well. It is, however, easily remedied, and requires only the fusion of six or seven ingots, with the requisite quantity of tin, together with some charcoal, and, if found necessary, poling the bath as in the refining of copper. All the oxides are thus reduced, and the alloy acquires a fine grain, and no bubbles appear in any part.

Some manufacturers introduce a small amount of iron into bronze in the founding; but experience has proved that this should only be employed in brass which is destined for small objects, as it gives to them hardness and tenacity, which are unnecessary in large castings. The quantity used should never exceed about 1 and 1½ per cent. of iron, and it should be incorporated in the form of white or tinned sheet-iron. Ferruginous alloy is

always less fusible than ordinary bronze, and on this account is less disposed to form cavities in the mass when cast in sand moulds, because the matter immediately solidifies upon the walls of the mould and does not allow the entrance of the air into the fluid mass, as is the case when ordinary bronze is cast under the same circumstances. With clay moulds however, this quality is unnecessary, because ordinary bronze does not comport itself in these moulds as when they are sand. Zinc is also alloyed with bronze in certain proportions, and communicates similar results.

Lead is not an advantageous ingredient in bronze, because it is readily oxidized, and hence augments the loss in the other metals by facilitating their combination also with oxygen; besides, it has a tendency of precipitating the copper with it towards the bottom of the casting, thus producing great inequalities if the object be large.

For many of the uses to which bronze is applied in the arts its composition is altered; thus, for wheel boxes or sockets the alloy contains—

| | |
|---|---|
| Copper, | 80 |
| Tin, | 18 |
| Zinc, | 2 |
| | 100 |

The fracture of this alloy is nearly white; it has a dry grain, and is very hard, but still may be worked. The zinc is added with the view of preventing cracks, which are apt to form in the casting owing to the contraction of the alloy upon cooling.

Another alloy intended for bearings has the following composition:—

| | |
|---|---|
| Copper, | 82 |
| Tin, | 16 |
| Zinc, | 2 |
| | 100 |

This is somewhat more malleable than the preceding, so that when the collar is being forced on to its place it is less liable to break.

An alloy, when required to resist powerful friction and sudden shocks, is made of the annexed proportions, namely—

| | |
|---|---|
| Copper, | 83·0 |
| Tin, | 15·0 |
| Zinc, | 1·5 |
| Lead, | 0·5 |
| | 100·0 |

For pump-boxes and balls, and such articles as require to be brazed or soldered, the proportions are—

| | |
|---|---|
| Copper, | 87 |
| Tin, | 12 |
| Antimony, | 1 |
| | 100 |

This alloy when broken presents a reddish fracture with a fine grain. It is malleable, but not sufficiently so as to answer for the material of stop-cocks, pump-valves, and the like, which are subject to receive concussions, &c. These are better when made of bronze containing—

| | |
|---|---|
| Copper, | 88 |
| Tin, | 10 |
| Zinc, | 2 |
| | 100 |

This alloy has a fine grain, and is capable of receiving a high polish; it has a reddish colour.

The furnaces used in bronze casting vary in shape according as the work to be done is large or small. For very large castings the furnaces are either completely circular or at least oval; but for ordinary work they are lengthened out as in figs. 5, 6, 7, 8,

Fig. 5.

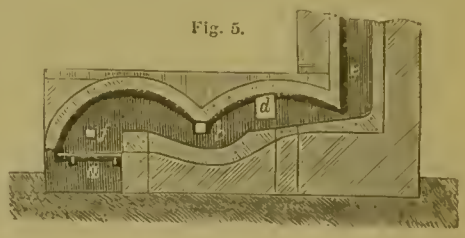



Fig. 6.

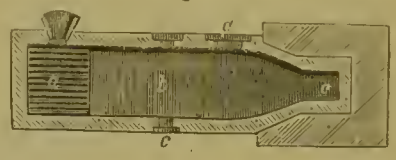



Fig. 7.

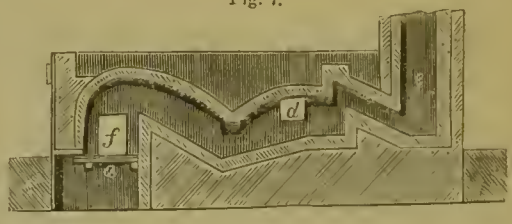



Fig. 8.




which depict the forms used ordinarily. The same letters apply to each figure:—*a* is the fire-grate; *b*, the hearth; *c*, the opening through which the melted metal is run off; *d*, the door through which the metal is introduced and worked; *e*, the flue leading to the chimney shaft: *f*, the fire door.

The bronze intended for medals is generally melted in small crucibles, and then cast in a mould made of sand. This is constructed of two parts or frames; the lower one, filled with the fine sand slightly moistened, is sprinkled over with ground charcoal, and the model either in wood or metal pressed down to half its thickness; the top of this is likewise covered with the powdered charcoal as before, and the superior frame pressed upon it, and secured in its place. Three small openings are formed in the sides of the

frame, by laying the one end of iron or brass wire against the model, the other passing out of the frames, all of which are withdrawn as soon as the frames are secured to one another. In one of these a small tube is inserted for the purpose of introducing the metal, and the other two serve for carrying any vapour from the interior during the drying, to which it must now be subjected. To expedite this part of the work, it would be well to use only as much material as will be sufficient to resist the action of the metal, and also it hastens the desiccation to have the exterior coating composed of coarse sand, for then the aqueous vapour escapes with greater facility. Another point of economy is to cast the model and the feeding jet in some metal which will be able to resist the pressure of the moulding frames, so as to avoid the inconvenience and injury which sometimes arise from the drawing of the wire already spoken of; in doing so however, one moulding is sacrificed, but the advantages gained compensate for this. Although charcoal powder may be effectually used for strewing over the moist moulding frames, finely-ground bone ash, powdered slate, and the like, may likewise be employed; yet the first is to be preferred when it can be conveniently obtained, because, being soluble in hydrochloric acid, it can be removed by this means from the medal, and thus its cleaning is performed with facility.

The other opening by which the moisture or other vapours flow out must always be formed with the wire. Both this and the jet should be proportionate to the size of the casting, more especially the latter. The jet can be made to communicate with the model in two ways: either by the lower part in the form of a siphon, or by the upper in the usual manner. When the siphon form is used, the metal must be cast at a higher degree of heat than in the other, because of the length it has to travel before it enters the mould; and although, by filling the latter from beneath, it allows the moisture and air to escape more freely than otherwise, yet the greater heat is productive of inconvenience by giving porous castings, which is not the case with the other kind of jet. Besides these mentioned, there is another difficulty to be contended with in casting the metal, and this is, that the cast has never that strict identity with the model, in dimensions and the particulars of outline, which it is necessary that it should possess. This arises from the circumstance that the metal, in the act of cooling, contracts very much, and therefore, when the casting and mould are placed adjacent to one another, a marked difference is visible; but after being submitted to the pressure of sinking the die, it becomes more apparent. It may, however, be remedied by making the mould sufficiently large to compensate for the contraction which takes place. An exterior coating of a different body to the model has been found to answer well; lead paper has been proposed, but on account of the inconvenience which it necessarily offers, it cannot be satisfactorily managed.

As a substitute, recourse is had to tinning the model, and although the coat thus deposited is very small, yet it is sufficient to make up for the contraction, and besides, it contributes to remove all the slight inequalities of its surface, which, unless prevented, would be impressed upon the casting. All these particulars being carefully noted and observed, the compound metal, which should be fused in quantities of 10 or 12 lbs. in crucibles, heated by preference in a small wind furnace, is poured into the moulds at such a degree of heat as will not injure their outline. This point can only be arrived at by practice, which may be assisted by the following particulars:—If the metal be too cold, it flows badly in the mould, and the casting appears pasty; if too hot, it will act upon the moisture of the sand, and disengage vapours which will give a blistered irregular surface to the object cast. When the metal is heated to its proper degree for casting, it is found coated with a layer of oxide which has a smooth even surface; if this be removed, and the metal examined, it appears of a brilliant white. If the heat be too feeble the oxide on the surface will not be smooth, but present an uneven tarnished appearance; on the contrary, if the temperature be too powerful, the oxide enters into fusion, and appears like the metal, quite luminous.

As soon as the moulds are filled, the castings should be removed with all possible speed, in order that they may be thrown into water for the purpose of annealing; if this be neglected, and they are allowed to cool, they must be again heated to give the tempering necessary for their being worked under the die. After the impression is received, they are again heated to regain the peculiar hardness and durability of the bronze.

This terminates the work of casting medals or coin, but before they are laid aside it is customary to give them the finish, in order to make them resemble the ancient bronzes. This is done by boiling the medals, &c., in a solution of chloride of ammonium and acetate of copper. A film of oxide of copper is thus deposited upon their surface, the colour of which is more or less intense, according to its thickness. If the composition of the medal be rich in tin this process is not very successful; should zinc also enter into it as a constituent it can be effected by rubbing the surface with a powder prepared of sand and a copper salt mixed. Sometimes this is prepared by taking the following proportions of the ingredients named as under, digesting the whole in a bath of dilute nitric acid, and applying the solution with a brush. The mixture for antique bronze is—

| | |
|---|---|
| Ordinary vinegar, | 0·90 |
| Chloride of ammonium, | 0·09 |
| Powdered green, | 0·01 |
| | 1·00 |

For Florentine bronze the ingredients are—

| | |
|---|---|
| Alcohol, | 0·80 |
| Red lead, | 0·20 |
| | 1·00 |

Digested as above described in dilute acid before being applied.

Gun Metal.—This variety of bronze is formed of 88 to 90 parts of copper and 9 to 12 of tin, and from these proportions the founder very seldom deviates, although the constitents must he varied according to the size and nature of the casting. It is absolutely necessary that the admixture should be quite pure, for the smallest admixture of sulphur, lead, iron, or arsenic, would cause serious injury, and probably render the cannon useless. Lead, when combined with copper and tin, forms a soft alloy greatly deficient in tenacity, which is liable to fuse at the temperature developed by the explosion of the charge in the gun, and thus to occasion inequalities which eventually destroy accuracy of aim. Again, if sulphur, arsenic, &c., be present, they render the alloy brittle, and consequently unable to withstand the shock of the discharge.

The absence of these substances does not, however, insure the freedom from serious defects which often arise from over-hardness and want of tenacity in the alloy. By augmentiug the quantity of the tin the hardness of the alloy is increased, but at the same time the homogeneousness of the alloy is more or less diminished when the weight of the alloyed metal exceeds a certaiu limit; since, although the two ingredients may be proportioned in the best possible way, yet during the casting the heavier metals gravitate to the bottom, giving rise to a more fusible compound in the superior part, which necessarily must contain more tin than it would do were the mixture homogeneous. This parting of the metals often occasions serious defects in the castings. When parts of the gun contain an excess of tin, and are consequently easily melted, these assimilate the sulphur in the gunpowder at the moment of explosion, and give rise to cavities of sulphide of tin which quickly occasions incrustations. Indeed, the most serious defects of cannon arise from the change which the metal undergoes in the mould. To some extent this evil has been overcome by the addition of 0·12 to 0·5 per cent. of phosphorus.

This defect is also to a certain extent remedied by cooling the metal to a certain point before allowing it to fall into the mould, and effecting the cooling by a certain period; the parting of the metals is thus in a great measure prevented.

Experience has proved that one alloy will not answer equally well for ordnance of all sizes. For eight-pounders, or thereabouts, that which is best adapted is made from 92½ parts of copper and 7½ of tin.

Considerable loss is sustained in bronze casting, and a great overplus of metal has to be used; this, however, is for the most part recoverable. It is laid down as a rule that, to obtain a casting of 100 lbs. weight, no less than 220 lbs. of material must be employed. It is disposed of in the following manner:—

| | Lbs. |
|---|---|
| Weight of casting, | 100 |
| Loss of bronze in the scoria, | 12·5 |
| Bronze wasted in the *debris*. | 107·5 |
| Bronze employed, | 220 |

The loss of metal and temporary waste being so great, it is evident considerable practice must be brought to influence the proper management of the work. For greater facility rules have been laid down, whereby the quantity of material required to be operated upon, in order to produce a certain weight of castings, may be ascertained by comparison. It is stated that in each charge one-tenth of its weight of new or ingot copper should be used, and that the tin in the shape of ingots should form about 15 per cent. of this quantity.

The subjoined numbers express the proportions which are to be used in the coustitution of—

| Lbs. | |
|---|---|
| 2200 | of casting, namely, |
| 488 | of ingot copper, |
| 73 | of ingot tin, |
| 1769 | of old pieces of bronze, |
| 2556 | of bronze in the waste attending the manufacture, |
| 4886; | total weight of the mixture employed. |

The real loss attending the manufacture, under ordinary supervision and with due care, does not exceed 10 per cent., and rarely indeed amounts to this, more frequently bordering on 6. It is evident from this that the furnace must be of such capacity as will work the increased proportion of metal where large castings are made.

The following table from Dumas shows the proportions which have been followed in the foundry at Toulouse for the manufacture of cannons:—

| | Siege guns. | | Field guns. | | Campaign guns | | Howitzers. | | Mortars. | |
|---|---|---|---|---|---|---|---|---|---|---|
| Calibre, | 24 | 16 | 12 | 8 | 12 | 8 | 24 | 6 | 10 | 8 |
| | pounds. | pounds. | pounds. | pounds. | pounds. | pounds. | pounds. | pounds. | pounds. | pounds. |
| Weight of furnace charge, | 13181 | 9812 | 7894 | 5336 | 5512 | 3748 | 4013 | 5556 | 5567 | 2324 |
| Weight of casting, | 8291 | 5821 | 4454 | 3153 | 2719 | 1883 | 3488 | 4932 | 5115 | 1883 |
| Weight of excess of metal used in casting. | 3528 | 2712 | 2359 | 1356 | 2159 | 1356 | — | — | — | — |
| Weight of waste in channels, &c., | 330 | 320 | 309 | 298 | 309 | 298 | 298 | 309 | 309 | 309 |
| Probable loss, | 1332 | 959 | 772 | 529 | 325 | 211 | 227 | 315 | 143 | 132 |
| Probable centesimal loss, | 9·8 | 9·7 | 9·7 | 9·9 | 5·6 | 5·6 | 5·6 | 5·6 | 5·6 | 5·7 |

Cornish and Banca tin are preferred, being generally free from lead. Sometimes the manufacturer employs old tin, which usually contains a large proportion of lead; but in this case it is necessary that it should undergo a process of refining before it can be incorporated with the other constituents of gun metal. This is done in a manner analogous to that described for separating copper and silver, and is based upon the greater fusibility of an alloy of lead and tin than of the latter alone. By gently

heating the metal in a reverberatory furnace the more fusible alloy of lead and tin will quickly begin to flow, leaving the most part of the tin behind and comparatively pure; this latter portion is then submitted to one or other of the usual methods for depriving it of traces of lead.

The materials being at hand and ready for fusion, the mould should be prepared so as to receive the metal when melted, to give it the proper shape. Much depends upon the proper construction of the moulds in getting the pieces free from defect. They should have sufficient solidity to prevent the melted metal altering them, and the air and other gases which are contained in them, or developed by the heated medium, should have ready means of egress; otherwise, if confined, they will either endanger the safety of the mould by their expansion, or render the casting vesicular and imperfect. The material employed is clay or sand. With these, a quantity of brick-dust, cow hair, and horse dung are incorporated, to give them tenacity, so that they may be able to resist the metal. Care should be taken that no lime or silicious oxide of iron enters into this mixture; because the first would cause the evolution of gaseous matters when the liquid metal comes in contact with it, and the other would enter into fusion; the defect of blistering would follow from the former, and loss of true outline would be the result of the latter.

The method of procedure is to grind the clay, or temper it very fine with the aid of moisture, and then mix four parts of this with one of dung, leaving the matter to rest for eight days or thereabouts. This loam is macerated with three-fourths of its weight of sand, to which about a sixth of hair has been added. Another mixture is composed of clay, two parts by measure, sand one, dung a half, and hair half a part, the whole being well commingled. In the preparation of this mixture, however, various proportions are taken by different parties, all of which may be suitable in certain cases.

Fine sand, mixed with gelatine or glue, is also used to communicate an even surface to the mould before depositing the wax upon it. This article is usually obtained by burning tanners' waste, and washing the ashes with water to remove alkalinity. The more distinct parts of the mould are constructed of a mixture of 2 parts of yellow wax and 1 of resin. After they are made in the usual manner, they are dried, so as to be ready to receive the melted metal.

Reverberatory furnaces are resorted to for making the alloy, of which two forms are in use. One of these has the hearth circular, while the other is of the elliptical shape. Wood is generally burned in those with a circular hearth, and coal in the other variety. Artificial blasts are not employed in either case; but the draught is increased as much as is required to generate the proper degree of heat, without admitting any oxygenous gases into the furnace, which would tend to scorify the metals. On this account the fire is situated in the arch of the furnace, and as a precautionary means the fuel is always kept in a thick stratum upon the grate, to deoxidize the air passing in for supplying the combustion. Some regard the furnaces with circular hearths as being more economical, on the ground that they hold more matter, and present a less surface than the other to the flame, and therefore the charge in them is less liable to oxidation than if the hearth were elliptical; also, that they produce a more cohesive bronze. On the contrary, it is acknowledged that the other effects the fusion of the charge more rapidly, and affords facilities for rabbling and poling, of which advantage cannot be taken in the foregoing; likewise, that it produces a more homogeneous alloy, and that the consumption of fuel is much less than in the round furnaces. When, however, much sulphurous matter is contained in the fuel, serious injury is caused thereby, inasmuch as it gives rise to the formation of sulphides of the metals, which render the alloy brittle and inelastic.

Figs. 9 and 10 show a modern furnace for melting gun metal. A is the hearth, which is constructed of fire bricks. The furnace bottom is broadest at *m*, somewhat narrower at *n*, and is reduced to one-half the breadth at *o*, under the arch. The fire-grate,

Fig. 9.

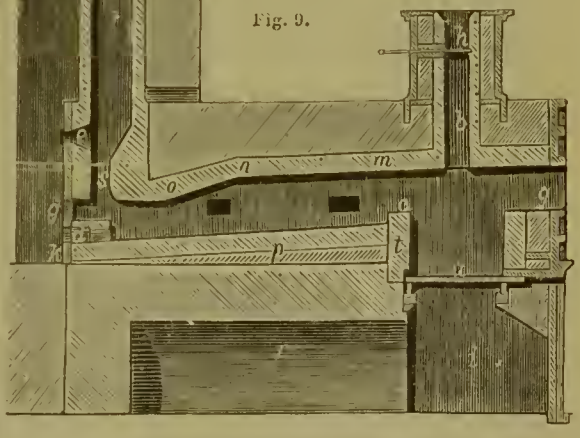
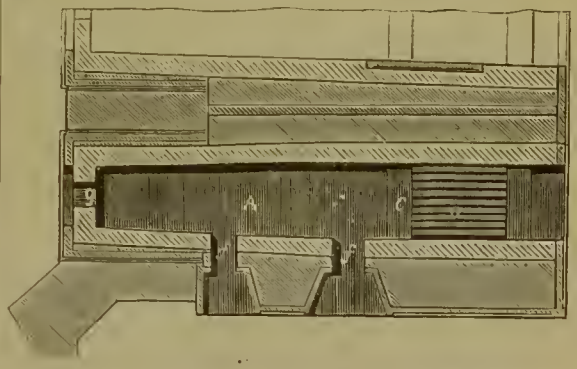



Fig. 10.



*a*, is furnished with broad fire-bars; *i* is the ash-pit; *b* is the flue: it has a sliding damper at *h*; *c* is the fire-bridge beneath the furnace arch; *p* is the furnace bottom, sloping towards *d*, the taphole through which the charge is run out: this is closed by a door, *k*, in which is the opening *g*, through which the melting gun metal is stirred up and poled; *e* is another open-

ing for occasional inspection of the charge; *s*, a channel supplying air to the furnace; *f f*, doors for removal of scoria, &c; *g*, an opening used when large pieces of metal have to be melted; *t*, the chimney shaft. Large pieces of metal are thrust in through an opening at *q*.

According to the extent of the foundry and the size of the castings, several furnaces, of various capacities, are requisite, the principal ones being destined for making the bronze, and the lesser for smelting the refuse matter of the manufactory, or purifying some of the substances which are to be operated upon. The three parts of the furnace which require especial attention are the fire, the hearth, and the chimney. With regard to the first of these, as already mentioned, the principal fact which deserves to be particularly noted is the regulation of the draught. One of the reasons for constructing the fire-door in the arch of the furnace is, that it may not interfere with the current of air passing through, which it would not fail to do if constructed at the side, as is customary in reverberatory furnaces. The ashpit is entirely inclosed with the same view, in order that the hot cinders which fall through the grate may not rarefy the current of air rushing to the fire, and cause a deficiency by this means from the actual volume necessary to maintain the proper temperature. To render this more effectual it should be rather spacious. The galleries, in like manner, should contract as they approach the fire, so that the current may be delivered as dense as possible.

The interior of the furnace in which the operation of smelting is conducted is generally composed of two planes, inclined towards the middle, thus offering by their intersection a cavity leading to the outlet through which the liquid alloy is drawn off when requisite. During the fusion the metal is watched and treated with the necessary attention through the doors already mentioned. A variable position and construction is given to the flues, according to the size of the furnace; their superior end borders upon the chimney, and their lower extremity is sloped, and partly dips into the molten bath, so that the flame has to traverse the whole surface of the hearth before its exit. It is needless to say that the entire surface of the interior of the furnace should be made of the very best refractory bricks, set in a cement which will likewise effectually resist the action of the fire. For greater security a coat of refractory lute is put on the interior superficies.

When the furnace is newly erected, or the luting is renewed, it retains a great deal of moisture, which necessarily should be expelled before operating upon the metals, otherwise, if allowed to remain, it would act injuriously upon the structure, causing it to crack and break in various parts. To effect the desiccation, the interior is filled with bricks, by piling them upon the hearth in such an open manner, that the flame and heated vapours from the fire will easily permeate the mass. The doors are closed by a few firebricks cemented together by mortar, and the fire, which may be of coal, wood, or charcoal, according to the kind of furnace, is then lighted. At first the heat should be very gentle, and as the excess of aqueous vapours is expelled, it may be gradually increased during eight or ten days, about which time it arrives at a white heat, which should be maintained for two days longer, or thereabouts. At the termination of this period it may be safely assumed that the whole is thoroughly baked. All the doors and other orifices are then opened, and the structure allowed to cool gradually. Sometimes it is necessary to repair the furnace by such a coating. This should be foreseen in its erection, and sufficient room left for the purpose. In the latter instance the baking need not be prolonged beyond three or four days.

The charging of the furnace follows the removal of the bricks from the interior by introducing, first, the ingots of copper, the fragments of old cannon, and other cupreous matters. As soon as these are liquefied the remainder necessary to make up the total, in the shape of scales and turnings from the hammer and lathe, together with the requisite weight of tin, is added. Before introducing these, however, it is customary to coat the hearth and the walls with moist cinders, in order to prevent contact of the bronze with the bottom and sides, to which, if this were neglected, it is apt to adhere. The mouth of the tap-hole is likewise closed with an iron plug coated with loam, so as to fit more accurately the orifice. In arranging the charge on the bed of the surface, the larger pieces are placed in such a position that they will receive most heat. Care should likewise be taken that the mouths of the flues are not blocked up. On the contrary, these should be left as free to act as possible; because the briskness of the combustion is dependent in a great measure upon them. On the Continent the furnaces are generally heated with wood, oak or beech being used according as the country will supply it, though in Belgium coal and coke is much used for fuel.

During the first few hours of the firing the heat is kept very moderate, so that the expulsion of the aqueous vapour, &c., may be very gradual. When the sole becomes heated the fire is urged more strongly, and the metal, which hitherto manifested no signs of its action, begins to assume an incipient redness. The flame, which also appeared dull and scarcely extended to the vent-holes or flues, at this time becomes brighter and more enlarged, so that it rises to their upper end. By maintaining this temperature the metal reaches a white heat, and very soon begins to melt in part, and so continues till, at the end of seven or eight hours, it is entirely liquefied.

In the course of the operation it is observed that the bronze which forms part of the charge, before it becomes fluid, appears incandescent, the tin oozes from all the pores in drops, which unite and stream to the hollow of the hearth, carrying only a small portion of copper with them in combination. The operator takes care that all the matter is perfectly liquefied, by stirring in any particles which might remain at the sides and bottom of the molten bath.

When he is satisfied that all is melted he thrusts a long pole of birch wood into the mass, and stirs it about just as in the refining of copper. This causes a violent seething, and brings both the metals into more intimate contact, thus insuring more perfect combination than if they were left unmolested. The bath is likewise rendered more fluid, on account of the ebullition raising fresh metal to the surface, where it meets with greater heat; and unless the action of the pole were prolonged the inferior layers would not be sufficiently liquid, because the superior one, being more expanded on account of its contact with the high temperature of the fire, is specifically lighter; it would preserve itself at the surface, unless the mechanical action of poling instituted currents which would force the matter at the bottom to the surface to receive an equal amount of heat.

When the whole is in perfect fusion, the temperature being very elevated, the workman skims carefully the scoria which has risen to the surface during the poling. The heat of the fire is still maintained by the repeated addition of fresh fuel. The rabbling, poling, and skimming engage the whole attention as long as scoriæ are thrown off; and when these are for the most part removed, the fire being still urged to its highest limit, the tin necessary to make up the proper composition of the bronze is projected into the bath in the form of small ingots, to facilitate its rapid distribution throughout the mass. During this time, and successively to the period of casting, the fire and the poling are made to exert their utmost influence in keeping the molten mass as liquid and as homogeneous as possible.

To determine the moment most suitable for running off the fluid metal is a very critical point, and one that requires much skill and practice. Generally it is raised to the highest possible temperature under the circumstances, and it is thought that the more elevated the heat is the better; but even this, it is reasonable to suppose, will have its limit. When the metal is nearly ready, the workman finds that the spar of wood with which he effects the poling will feel light in his hand. It can then be thrust with facility into the bath, and its end will glide freely upon the bottom of the furnace. When withdrawn it retains very little metal, the chief portion falling off in small drops. The sound of the agitated matter is very clear. It may readily be thrown into numerous undulations, which as quickly subside. Fragments of lighted charcoal which float upon the mass move about very rapidly, especially towards the bridge of the furnace. Whenever a fresh supply of wood is thrown upon the fire it does not cause a disengagement of gases from the bath, but the flame which escapes by all the flues possesses a brilliant whiteness.

Preparations for the castings are being made five or six hours previous to the time in which this is to take place. The channel by which the fluid metal flows to the moulds is coated with loam and baked, first with a fire of wood and afterwards with one of charcoal or coke. The moulds must be left partly uncovered, so as to permit the escape of moisture more freely. These and the canal attached are carefully brushed, so as to remove all dust and extraneous particles of matter.

The iron plug which secured the tap-hole is then removed by appropriate means, and the metal allowed to flow out into receptacles in the channel, whence it is permitted to run into the moulds in succession till they are filled. During this part of the work much aqueous vapour and gases are disengaged by the superheated metal coming in contact with the mould, and cause great inconvenience and injury to the casting: their development may be prevented to some extent by taking care that no moisture can reach the mould by infiltration, and also by deferring the casting whilst the metal is too hot. When the jet appears of a bluish colour the material is highly fluid; but when it is bordering upon the point of congealing it assumes a violet tint, arising from an envelope of a yellowish-red, and is owing to a part of the metal solidifying. The vapours given off are apt to cause irregularities in the casting, if these were not prevented by pouring more metal into the inlets and keeping them quite full. It is customary, likewise, to throw some charcoal upon them, to keep them in a fluid state as long as any disengagement takes place, so that the metal in them may supply any vacancy caused either by the evolution of gas or the contraction during the cooling. After the metal has sufficiently congealed the partitions of the channel are removed, and likewise the brickwork and other appendages which were employed as means of security in the moulding; and after two or three hours the clay surrounding the casting at the top may be taken away, either wholly or in part. At the end of forty-eight hours or so, according to the size of the objects cast, they may be drawn, the earth and other extraneous matters being previously removed to the adjoining compartment. Owing to the pressure which is exerted upon the moulds, much metal percolates them. This is afterwards recovered by smelting those parts in which it is contained in a small furnace devoted to this purpose. The various other products of the channels, and the excess of material appended to the objects, are subsequently used up with another charge.

The guns are next treated by mechanical agency to give them a smooth exterior, and then bored in the usual way, and finally proved by various tests. The mode of proceeding above described applies equally to the casting of bronze in general.

Though steel has to a great extent superseded bronze in the manufacture of cannon, yet the cheapness and the facility with which guns can be made by casting in comparison with welding have led to many endeavours on the part of continental military engineers to increase the toughness of gun metal, so that it might be able to bear greater charges of powder.

In Russia experiments were made on the increased strain bronze was able to bear if it had been subjected to pressure whilst still in the liquid state. Guns of chilled bronze were exhibited at the Vienna

exhibition, 1873, by Lavessière, of Paris. The "chilled bronze" was, however, found to be deficient in elasticity and hardness. To overcome these defects General Von Uchatius, director of the Imperial Arsenal at Vienna, proposed to roll the chilled bronze, or rather gun metal, when cold. The results of his experiments showed that it was possible to roll the chilled bronze when cold up to an elongation of 100 per cent. without the least crack being made; and that with an elongation of only 20 per cent. the alloy obtained the hardness, elasticity, and strength of steel. The gun metal thus treated contained 90 parts of copper to 10 of tin, and was subjected to a pressure of 80,000 kilos. immediately after it had been cast into moulds.

These experiments brought to light a fact of high importance in metallurgical industries, viz., that the elasticity of all tough materials increases rapidly after they have been subjected to a force exceeding the elastic strength of the material. Thus, chilled bronze reaches its elastic limit under a strain of 100 kilos., corresponding to an elongation of 0·0004 of the original length; whilst after having been submitted to a tension corresponding to a permanent set of 0·004 of the original length the elastic limit of the material is raised to 1600 kilos., with a corresponding elastic elongation of 0·00192 of the original length. After a careful consideration, General Von Uchatius decided that the work done by the powder in the powder-chambers to the detriment of the guns might be anticipated in the manufacture of the gun by compressing the interior of the bore mechanically to a degree exceeding that produced by the explosion of the powder, and thus raising the elastic limits of those portions which have to resist the force of the explosion; *i.e.*, the material about the bore might be treated in a manner analogous to the rolling process above spoken of, until the requisite degree of hardness was obtained.

The bronze alloys best suited for cannon he found to be:—

| | | | |
|---|---|---|---|
| 10 | per cent. tin, | 90 | per cent. copper. |
| 8 | " | 92 | " |
| 6 | " | 94 | " |

Moreover, uniformity of quality throughout the casting was attainable by simultaneous inside cooling, *i.e.*, by the chilling of the bore. A current of air and a stream of water having respectively proved unsuitable for this purpose, solid cores of various metals were tried, and it was at length found that by using wrought-copper cores of 50 mm. diameter, perfectly good and reliable results could be attained.

The mode of gun-making at last adopted is as follows:—Guns of the desired size are cast in iron moulds in the ordinary way, but have their core "chilled" by a copper core. These hollow ingots are then bored out to a calibre of 80 mm., with an outside diameter of 260 mm., and are each 300 mm. long. At one end, the outside is turned to a diameter of 180 mm., corresponding to that of a finished field-gun, and the hollow ingot placed vertically upon a circular base-plate with a corresponding hole, and a conical piston of hardened steel forced through the tube by means of a powerful hydraulic press. As the tube opposes a resistance which increases with the widening of the bore, the difference in the diameters of the conical pistons following each other has to be reduced accordingly; so that with six pistons forced through the bore, the first one has a diameter 2 mm. larger than that of the bore, whilst the last is only ½ mm. larger than the preceding one. By this process the bore, which originally had a calibre of 88 mm., is enlarged 2 per cent. Its surface, when tested with the compressor, shows a hardness equal to that of gun-steel, and it was also observed that at the turned portion of the tube the interior had acquired the same hardness as the rest of the bore.

A gun thus constructed was fired 1800 times with the full service charge, without the least alteration being perceptible in its dimensions and general appearance, or in its shooting powers.

This mode of manufacture possesses the additional advantages that by it all unsound parts are easily detected, for wherever there exists a fault in the material, or where the bronze is not of perfect quality, the act of drawing immediately produces cracks and fissures. Another highly important point is the fact, that after the piston has been forced through the bore, the diameter of the latter contracts to 0·004 of the diameter within the elastic limit, proving that the different parts of the gun are in a state of elastic compression, which equals, according to careful calculations, a radial central pressure of about 2400 atmospheres. To prove this elastic compression to be acting throughout the whole mass, General Von Uchatius had a ring turned off one end of the tube until a small circle of metal on the inside of the tube alone kept the ring on the main tube. Before the chisel severed this last connecting circle, the ring spontaneously sprang off, and showed a smaller calibre bore than the tube from which it was taken.

The 8 per cent. bronze appears to be the best suited to the manufacture of guns, as the inner chilling can be effected much more easily than with the 10 per cent. bronze, and does not require the addition of so much copper as the 6 per cent. bronze. It is also the cheapest of these three alloys.

Guns manufactured as above described can be compared to coiled steel tubes, as they have the same degree of hardness, homogeneity, and strength in the bore as the latter, and as the radial pressure to the centre of the gun is obtained beforehand by the treatment of the material itself.

The quality of the bronze varies from the outside to the bore in direct proportion to the stress the gun has to bear. The elasticity of the inner parts and the toughness of the outer surface are far greater than that of steel.

The neutral axis, where the explosive force of the charge and the opposing elastic pressure of the material are in equilibrium, lies very near the bore in steel-bronze guns. To make such a gun fly to

pieces the elasticity of the whole material must be overcome simultaneously, and then the great toughness of the outer portions, bearing extension to 70 per cent. without breakage, would still offer opposition to the explosive force. In coiled guns, on the contrary, the neutral axis lies between the tube and the coils, and the latter have to bear the full force of the explosion.

TABLE SHOWING THE RESULTS OF TESTS WITH THE DIFFERENT MATERIALS FOR THE MANUFACTURE OF ORDNANCE.

| Load in Kilogrammes, per one Square Centimetre of Section. | Cast-iron frame, 9-inch gun. | | Bronze. | | | | | | Wrought iron from Styria in rods of small section. | | Krupp steel from 6-pounder. | | Steel-bronze near the | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Common form of 8-pounder. | | Chilled. | | | | | | | | Bore. | | Outside. | |
| | | | | | Cast. | | Rolled. | | | | | | | | | |
| | Elastic. | Permanent. | Elastic. | Permanent. | Elastic. | Permanent. | Elastic. | Permanent. | Elastic. | Permanent. | Elastic. | Permanent. | Elastic. | Permanent. | Elastic. | Permanent. |
| 100 | 2 | 0 | 10 | 0 | 8 | 0 | 2 | 0 | 4 | 0 | 1 | 0 | 3 | 0 | 3 | 0 |
| 200 | 10 | 0 | 15 | 0 | 15 | 0 | 7 | 0 | 9 | 0 | 3 | 0 | 5 | 0 | 14 | 0 |
| 300 | 15 | 0 | 25 | 0 | 25 | 0 | 10 | 0 | 11 | 0 | 7 | 0 | 8 | 0 | 25 | 0 |
| 400 | 22 | 0 | 35 | 0 | 40 | 0 | 22 | 0 | 14 | 0 | 12 | 0 | 14 | 0 | 35 | 0 |
| 500 | 27 | 0 | 47 | 1 | 53 | 2 | 37 | 0 | 18 | 0 | 16 | 0 | 20 | 0 | 55 | 0 |
| 600 | 33 | 0 | 56 | 4 | 62 | 4 | 50 | 0 | 22 | 0 | 20 | 0 | 26 | 0 | 65 | 0 |
| 700 | 38 | 2 | 66 | 7 | 70 | 6 | 60 | 0 | 24 | 0 | 25 | 0 | 33 | 0 | 78 | 0 |
| 800 | 47 | 4 | 77 | 11 | 79 | 8 | 73 | 0 | 27 | 0 | 30 | 0 | 40 | 0 | 86 | 3 |
| 900 | 51 | 5 | 88 | 20 | 87 | 10 | 86 | 0 | 31 | 0 | 34 | 0 | 48 | 0 | 93 | 7 |
| 1,000 | 61 | 6 | 101 | 32 | 100 | 13 | 96 | 0 | 35 | 0 | 39 | 3 | 54 | 0 | 103 | 12 |
| 1,100 | 68 | 8 | 110 | 52 | 108 | 22 | 107 | 0 | 37 | 0 | 44 | 5 | 60 | 0 | 112 | 18 |
| 1,200 | 76 | 10 | 120 | 96 | 115 | 47 | 117 | 0 | 40 | 2 | 50 | 7 | 66 | 0 | 129 | 26 |
| 1,300 | 84 | 14 | — | — | 130 | 117 | 128 | 0 | 42 | 3 | 55 | 10 | 73 | 0 | 135 | 45 |
| 1,400 | 92 | 19 | — | — | 150 | 327 | 139 | 0 | 45 | 4 | 60 | 14 | 80 | 0 | 160 | 125 |
| 1,500 | 101 | 24 | — | — | 170 | 380 | 149 | 0 | 48 | 5 | 65 | 20 | 88 | 0 | — | — |
| 1,600 | 110 | 30 | — | — | 192 | 441 | 159 | 0 | 52 | 6 | 71 | 31 | 95 | 0 | — | — |
| 1,700 | 120 | 35 | — | — | — | — | 170 | 0 | 57 | 7 | 76 | 38 | 102 | 0 | — | — |
| 1,800 | 130 | 50 | — | — | — | — | 179 | 2 | 62 | 8 | 81 | 48 | 110 | 0 | — | — |
| 1,900 | 142 | 65 | — | — | — | — | 193 | 5 | 67 | 8 | 85 | 120 | 115 | 2 | — | — |
| 2,000 | 157 | 81 | — | — | — | — | 203 | 8 | 72 | 9 | 90 | 252 | 121 | 3 | — | — |
| 2,100 | — | — | — | — | — | — | 215 | 10 | 77 | 10 | 98 | 360 | 127 | 5 | — | — |
| 2,200 | — | — | — | — | — | — | 222 | 12 | 82 | 12 | 110 | 586 | 134 | 7 | — | — |
| 2,300 | — | — | — | — | — | — | 239 | 14 | 88 | 14 | — | — | 142 | 8 | — | — |
| 2,400 | — | — | — | — | — | — | 252 | 18 | 93 | 16 | — | — | 152 | 10 | — | — |
| Elongation in 0·00001 of original length. | | | | | | | | | | | | | | | | |
| Absolute strength, | 2420 | | 2260 | | 3050 | | 5066 | | 4700 | | 4800 | | 4875 | | 3300 | |
| Limit of elasticity, | 600 | | 400 | | 400 | | 1700 | | 1100 | | 900 | | 1800 | | 700 | |
| Elongation in per cent. of original length, At the limit of elasticity | 0·033 | | 0·035 | | 0·040 | | 0·170 | | 0·037 | | 0·034 | | 0·110 | | 0·075 | |
| Elongation in per cent. of original length, At rupture, | 0·40 | | 15·0 | | 40·0 | | 22·0 | | 22·4 | | 21·4 | | 2·5 | | 40·0 | |
| Section at point of rupture, | 0·96 | | 0·66 | | 0·54 | | 0·96 | | 0·62 | | 0·50 | | 0·96 | | 0·58 | |
| Hardness (length of chisel-cut), | 10·2 | | 12·5 | | 12·5 | | 10·2 | | 10·5 | | 10·5 | | 10·5 | | 12·0 | |
| Number of blows of 1·2 kilogrammes required to break a test-bar with a sectional area of ·5 sq. centimètres, | 1 | | 1·10 | | — | | — | | — | | 209 | | 255 | | 146 | |

The bronze-melting furnace in use at the Royal Foundry at Munich, for casting statuary and objects of art, is shown in Figs. 11 and 12. Fig. 11 is a vertical section at $x$, fig. 12. Fig. 12 a horizontal section, along the line $y\,y$, fig. 11. The same letters apply to each engraving. The fire grate is at $a$; $b$ is the melting hearth, $c$ the outlet for the melted metal, $d$, opening for carrying off the products of combustion, $e$ the founding pit, $f$ the smoke shaft, and $g$ the charging door.

Phosphor Bronze.—Combinations of phosphorus with copper, zinc, or other metals, have long been known, but it is only since the carefully conducted and very exhaustive experiments of Messrs. Montefiore and Künzel, in 1869 and 1870, at Liége, have been completed that phosphor bronze, an alloy of copper, tin, and phosphorus, has become known and applied to art and industry.

From the description of bronze founding it may be gathered that there are several well-defined difficulties in making a uniform alloy. These are:—(1) Impurities in the metals, which seriously affect the physical properties of the copper. (2) Oxidation to variable extents, occurring in the melting. (3) Absorption of oxygen, or combination or admixture of oxides with the alloy, produced during the melting from the constituent metals, or their combination with minute doses of carbon or sulphur. (4) Evolution of oxygen (possibly of other gases) and expulsion of the oxides more or less during the cooling of the alloy, rendering it porous or "blown." (5) Segregation in cooling of the normal alloy, if attained (17 Cu + Sn. = 90·2 Cu + 9·88 Sn), into several alloys, some brittle, some soft, unequally diffused through the body of the casting.

The first has practically vanished through metallurgic improvements. The second must remain a difficulty always, only to be mitigated by operating upon a very large scale, and always with furnaces

the same in construction and working, and with the same fuel. The third and fourth are to a great extent met by the introduction of phosphorus into the alloy; whilst the fifth and last may undoubtedly be much lessened, if not removed, by casting the objects in massive iron moulds, instead of those of loam, so as to "chill," or suddenly cool, and solidify the alloy, before time has been given for its degregation.

Copper and phosphorus combine with facility at temperatures sufficiently high to secure intimate contact of the two elements. By carefully dropping phosphorus on melted copper in a crucible the metal may be made to take up as much as 11 per cent. The fusibility of the copper is much increased, and

Fig. 11.

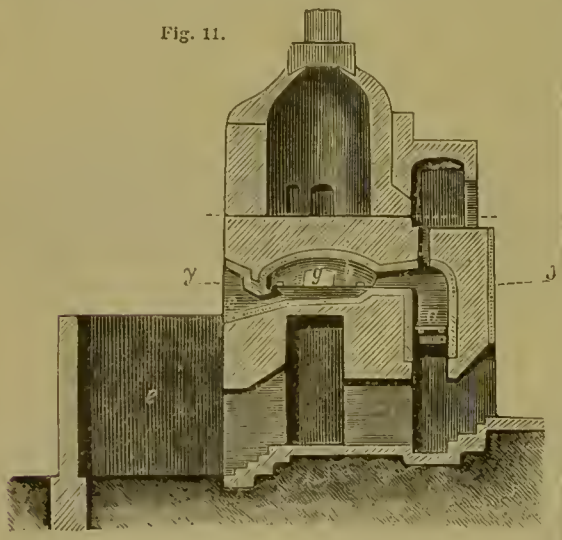
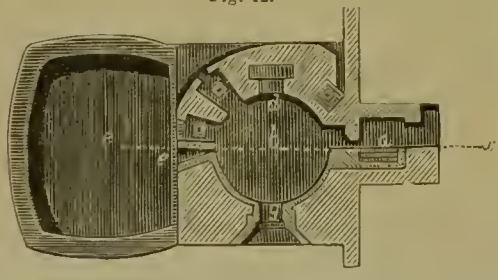


Fig. 12.



it becomes at the same time so extremely hard that it can scarcely be touched by a file.

Copper phosphide was first formed about the middle of last century by Macquer, and somewhat later studied by Bertrand Pelletier, and also by Sage. The latter states that 92·3 parts copper and 7·7 phosphorus is a stable if not a definite compound, hard and brittle, and with the grain and colour of steel, and that with much less phosphorus the combination is malleable and yellow, so that, say Aiken ("Chemical Dictionary," 1807), "it may be hereafter found useful in manufactures." H. Rose formed three or four definite phosphurets of copper, and described their properties in "Pogg.'s Ann.," vols. iv. xiv. xxiv. Berthier ("Essaies," tome ii.) restudied the subject, and described some of the properties of these compounds. Percy ("Metallurgy," vol. i.) formed some of them, and has described their properties. Shroeter also prepared compounds of copper and phosphorus which he considered to be definite phosphides. These were dicupric phosphide, $Cu_2P_2$, which he believed he obtained by reducing dicupric phosphate by passing hydrogen over it. When mixed with chlorate of potash and sulphide of copper, or pounded coke, to increase its conducting power, dicupric phosphide forms the fuse compound which Professor Abel has found best suited for firing charges of gunpowder by magneto-electricity.

Tricupric phosphide, $Cu_6P_2$, was stated by H. Rose to be produced by passing phosphuretted hydrogen over heated copper protochloride, or into a solution of sulphate of copper. The first process yields it as a black powder, the second as a black flocculent precipitate, which on heating in vacuo assumes the red colour of precipitated copper. Tricupric phosphide is more fusible than copper, but does not melt at the fusing point of glass.

Tricuprous phosphide ($Cu_3P_2$) is obtained by passing phosphuretted hydrogen over cuprous chloride. It is a black powder, which after strong ignition turns grey, and assumes a metallic lustre.

Professor Abel has confirmed Rose's experiments with regard to the phosphides $Cu_6P_2$ and $Cu_3P_2$, and has shown that the dicupric phosphide cannot be produced by the action of hydrogen on the diphosphate, the proportion of phosphorus in the product, after separation of the phosphoric acid, being between 3 and 8 per cent.

He also found that dicupric phosphide ($Cu_2P_2$) is converted into hexcupric phosphide ($Cu_6P_2$) by ignition, either alone or in hydrogen gas. The hexcupric phosphide contains 14 per cent. of phosphorus.

Phosphorus vapour passed over copper at a low red heat causes incandescence, and forms a fused mass of a steel-grey colour, which contains 12·2 to 13·5 per cent. of phosphorus.

By adding phosphorus to fused copper, and stirring the mass till it is nearly cold, a product is obtained consisting of three layers, the uppermost being white, very hard, and brittle, with shining crystalline fracture, and containing from 7 to 12 per cent. of phosphorus; the middle layer being grey, with granular fracture, and containing 4 to 6 per cent. phosphorus (this forms the principal part of the whole mass); while the lowest, which is insignificant in quantity, consists of nearly pure copper, containing only 0·5 per cent. phosphorus.

By adding phosphorus to copper, melted at such a temperature that part of it still remains solid, Abel produced a compound containing from 2 to 4·7 per cent. phosphorus, which by casting in iron moulds he obtained in homogeneous hard masses, having a fine-grained fracture, like that of bell-metal, but quickly tarnishing. By fusing this compound with pure copper, other compounds, containing smaller proportions of phosphorus, were obtained, which exhibited greater tenacity than ordinary gun metal.

In 1865 Abel published the results which he had obtained in the Woolwich Arsenal Laboratory (*Chemical News*, vol. xii. p. 172, and "Report of the British Association," 1865). These compounds were tested as to tensile strength at the arsenal with the following results:—

Resistance per Square Inch to slowly applied Strains.

| | Lbs. per square inch. |
|---|---|
| Gun bronze, | 32,000 |
| Copper, | 25,000 |
| Copper + 0·5 per cent. phosphorus, | 38,389 |
| Copper + 1·4 per cent. phosphorus, | 47,000 |

The mode of casting has, however, considerable influence on the physical properties of the phosphoretted copper. Abel found that copper containing 1 per cent. of phosphorus when cast in an iron mould exhibited a tenacity of 36,893 lbs. to the square inch, whereas when cast in a sand mould its tenacity was only 13,959 lbs. to the square inch. Altogether he considered phosphoretted copper as not adapted for casting, as it contracts very much in solidifying, and when cast in moulds of sand or loam the casting is very porous. By fusing the phosphoretted copper with iron, the greater part of the phosphorus is removed with formation of iron phosphide, which separates as a distinct layer, while the copper becomes alloyed with iron.

Mr. Abel does not appear to have followed up his research by investigating the compounds of bronze and phosphorus, and has not published any further experiments, though in a communication to the War Office, dated June 27, 1870, he stated that he had subsequently to his experiments above, made some on phosphorized bronze, and "that the properties of the material were of a very promising nature." Mr. Parkes, of Birmingham, about this time took out two patents for the employment of phosphorized copper and *brass*. He does not mention *bronze*.

In 1854 M. Rucolz, of the Orleans Railway, observed the great increase of tenacity and resistance to abrasion given to bronze by phosphorus, and in 1856 had some 4-pounder bronze guns cast containing 0·6 per cent. of phosphorus; these were experimented on by the French artillery with, on the whole, favourable results.

Between 1868 and 1870 Messers. Montefiore-Levi and Künzel engaged in experimental researches on the improvement of gun bronze, which embraced the following heads of research:—Binary alloys of copper with manganese and with nickel. Ternary alloys of bronze with nickel, iron, and zinc. Combinations of phosphorus with copper and with bronze.

As regards the purity of the several metals employed, the copper was either "best selected" from Pascoe, Grenfell, & Co., Swansea, or punchings from the plate-copper of locomotive fire-boxes. The tin was Banca, or that specially purified at the works of Val Benoit, whence also came the nickel, which, except a trace of sulphur and 0·3 per cent. of iron, was chemically pure. The manganese alloys were formed from a manganiferous copper of ascertained constitution produced by the reduction of the mixed oxides of copper and manganese, both being pure, in a cupola, which, we may remark, must have contained a sensible quantity of carbon and of other bodies if the cupola fuel was coke. In the phosphorus experiments, that body was brought into combination either in the state of a previously formed rich phosphuret of copper or one of tin. The alloys were all melted in plumbago crucibles under a covering of charcoal. Analyses of the alloys formed showed the extreme difficulty of procuring, after casting, alloys of predetermined constitution; in some cases as many as ninety proof pieces were cast before one was obtained having the assigned constitution within limits of one-tenth per cent. The proof bars were cast in a two part, nearly cylindrical, cast-iron ingot mould, weighing about 170 lbs., and producing a very slightly conical ingot, with an enlargement at the head, of about 19 in. long by about $2\frac{1}{4}$ in. diameter. From these cylindric bars for testing, provided with shoulders to be gripped at both ends, were turned, each of very nearly 1·10 in. diameter, by 10·50 in. length between the shoulders.

The important question, first entered upon by Dussaucoi, of the effects of pouring alloys such as these at different temperatures, and cooling them at different rates, was inquired into with a good deal of care. They determined the temperature of the liquid metals at the moment of pouring by casting into a known weight of water at a known temperature, a given weight of the liquid metal whose composition was assumed known, and the specific heat of its constituents also. Then, from the equation

$$x = \frac{P^1 (t^1 - t)}{P c} + t_1$$

in which $P^1$ is the weight of water; P, that of the fluid metal cast into it; $t$ = the temperature of the water before, and $t^1$ that after the casting into it, the temperature of the liquid metal was calculated. This is, in fact, the "method of mixture" in which, knowing the specific heats, we can find the temperature, or *vice versâ*. Though this equation did not afford precise results, it was, however, the only method practically available, and the results are valuable as an instalment upon an almost previously untouched matter of precise inquiry.

The "liquation" or segregation of these alloys was ascertained by melting 10 kilos. of each alloy in a plumbago crucible, permitting the liquid metal to cool until a crust formed; then breaking this and pouring out from the surrounding metallic shell the liquid contents. The crucible and shell were then further slowly cooled; and if, prior to complete solidification, a further segregation took place from the shell, it was poured out, and all these different alloys were submitted to analysis.

The experiments made upon ordinary gun-metal were as follows:—

Bronze which when first alloyed contained—

| | Tin. | Copper. |
|---|---|---|
| Metal (originally), | 10·10 + | 89·90 |
| After one remelting, contained | 9·82 + | 90·18 |
| " two " " | 9·40 + | 90·60 |
| " three " " | 9·16 + | 90·84 |
| " four " " | 8·52 + | 91·48 |

As regards the change of composition due to repeated melting, the tin thus continually decreases in relation to the copper by oxidation; and assuming, as we are justified in doing, that some of the oxide of tin is involved *as oxide*, if not combined *as such* with the alloy, the actual amount of *metallic* tin present in each case is *less* than that assigned by the above table—which, as deduced from analysis, gives the *whole* of the tin present in the alloy, in whatsoever state.

The experiments made in the segregation (*liquation*) of the ordinary bronze into different alloys in slow cooling generally agree with what had been already indicated by Dussausoi and Mallet. The results of these experiments are, that ordinary bronze, by slow cooling, segregates into several different alloys; that richest in copper first. Those subsequently segregated, the authors think, have not any constant constitution. Finally, there is segregated an alloy of nearly constant constitution, which approaches to that of 18 per cent. of tin and 82 of copper.

The manganesiferous alloys they concluded to be wholly useless for gun metal, as indeed those of nickel and of iron likewise, though in certain proportions they present very high coefficients of rupture. But the ready oxidability of manganese at high temperatures as compared with copper produces such uncertainty in the results that, independently of their expensive character, these alloys have not come into use, though it is proved that manganese does exalt the hardness and elasticity of bronze.

As to nickel, they found its alloy with copper more absorptive of oxygen than copper itself, and they could only with difficulty obtain some sound test bars, containing a low percentage of nickel, by casting the alloy in a red-hot ingot mould. It is a remarkable fact that nickel in large proportions should play the same part that tin does when either is alloyed with copper, in causing the compound to absorb oxygen when in fusion and give it up on consolidation. Copper with 20 per cent. or more of bell metal is far *more* absorptive of oxygen than copper itself; and it has been observed that when large bells are cast from nearly pure copper and tin, they are always more or less full of microscopic vesicles, whilst a very small percentage of zinc and of lead present seems to prevent this.

In the ternary alloys of bronze with nickel the physical effects of the latter metal are not striking, and the results as to tension not promising. And, as respects bronze with iron, these results are not more so, resulting from the far more rapid oxidability of iron at high temperatures, than either of the other two metals present.

The addition of minute doses of zinc to ordinary bronze (2 per cent.) they found augmented the resistance to rupture (by reducing involved oxides), but it softens the alloy, and causes it to lose its elasticity with great rapidity when near the elastic limit.

The beneficial part which zinc plays is, like that of phosphorus, that of a deoxidant, and it was simply as such that Montefiore-Levi and Künzel first proposed to themselves to employ it. Finding, however, that phosphorus in higher proportions sensibly hardened as well as increased the tenacity both of copper and of bronze, they added larger doses.

In remelting old bronze there is much difficulty in determining analytically the proportion of oxides, or of oxygen, mixed up or combined with the metal, and it has been found that the more oxide was thus enveloped the less was the amount of segregation in cooling; also, that *brassage*—that is, stirring about (as in "poling" copper) a large mass of old bronze remelted, and without charcoal covering, in the furnace with a pole of wood (generally of birch unseasoned)—has but slight effect in eliminating the oxide; and here comes in for the first time the application of phosphorus. By its introduction in extremely feeble proportion indirect evidence is afforded that oxygen *is* involved in some form in the remelted bronze, and Montefiore-Levi and Künzel argue, that it exists in the metal not as occluded oxygen, but as oxide of tin. In whatever be its state, the addition of a feeble dose of phosphorus appears to remove it, if not completely, yet much more completely than any amount of poling (brassage); so that whilst the elastic and rupturing resistances of old bronze containing very much oxide were exalted from 3 to 8·5 per cent. by brassage, these were increased from 9 to 36 per cent. respectively by the addition of only about as much phosphorus as eliminated the oxygen or oxide.

Shavings of old bronze were melted, and a bar thereof cast at 1595° C. The remaining liquid bronze was stirred with a wooden stick (poled), and a second bar cast at 1668° C. The remaining metal was deoxidized with phosphorus and a bar then cast at 1614°. The three castings were thus made out of the same crucible and in the same manner into three iron moulds. The results were as follows:—

| Nature of the Bronze. | Absolute Resistance. | Elastic Resistance. | Lengthening until Rupture. | Diminution of Section. |
|---|---|---|---|---|
| | | | Per Cent. | Per Cent. |
| Old bronze,..... | 1613 | 1209 | 2 | 3·2 |
| Old bronze, poled, | 1755 | 1244 | 2·8 | 3·2 |
| Old bronze deoxidized with phosphorus,..... | 2384 | 1356 | 6·8 | 6·7 |

Thus, by the entire reduction the old bronze has tripled its tenacity and considerably augmented its absolute resistance.

Having so far succeeded in eliminating the oxides from the bronze, the inventors showed that, by the further addition of from 0·1 to 5·2 of phosphorus to the bronze alloy, the qualities of the latter become more and more changed, the colour becomes evener, the grain or fracture finer, and the elasticity and resistance to strain and compression are considerably increased; it attains a great fluidity when melted. As minute quantities of carbon alter the physical properties of iron, so a minute quantity of phosphorus so changes the character of bronze that

what steel is to wrought iron, phosphor bronze is to ordinary bronze.

Phosphor bronze is manufactured commercially by the admixture of copper phosphide or tin phosphide, with the required quantities of melted copper and tin. The smelting furnaces are similar to those used for smelting bronze or brass.

The bronze is first melted, and then the copper or tin phosphide (by preference the latter) added, little by little, with much stirring.

This phosphide, $Su_3P$, containing 6 per cent. phosphorus, is prepared by gently heating together phosphorus and spongy tin in a tightly-closed crucible. The spongy tin is prepared by precipitating a solution of tin chloride with metallic zinc. The phosphorus is first placed at the bottom of the cold crucible, which is then filled up with moist precipitated tin. Heat is applied until fusion takes place, and no more phosphorus flame appears. On cooling, the tin phosphide is found in large crystals, which have a melting point much above that of pure tin.

The qualities of phosphor bronze have been largely tested and tabulated by Montefiore-Levi and Künzel.

| Cast Metal. | Diminution of Section before Rupture. | Resistance in lbs. per square inch. | |
|---|---|---|---|
| | | Elastic. | Absolute. |
| | Per Cent. | Lbs. | Lbs. |
| Pure copper, ..... | 3·30 | 4·4000 | 6·975 |
| Ordinary gun metal, containing 9 parts copper, 1 part tin, ..... | 3·60 | 12·800 | 16·650 |
| Phosphor-bronze,* ..... | 8·40 | 20·500 | 56·945 |
| " ..... | 1·50 | 24·700 | 46·100 |
| " ..... | 33·40 | 16·100 | 41·448 |
| " ..... | 3·53 | 55·800 | 74·966 |
| " ..... | 3·20 | 55·200 | 73·987 |
| " ..... | 9·40 | 40·500 | 63·653 |
| " ..... | 31·30 | 26·300 | 54·060 |
| " ..... | 59·10 | 21·700 | 50·120 |

In the imperial arsenal at Vienna experiments were made by General Von Uchatius, giving the following results:—

| | Absolute Resistance. | Point of Elasticity. | Stretch in Percentage. |
|---|---|---|---|
| | | | Per Cent. |
| Phosphor bronze, | 5660 kilos. per sq. c.m. or 81,795 lbs. per sq. inch, ..... | 3800 kilos. per sq. c.m. or 54,915 lbs. per sq. inch, ..... | 1·6 |
| Krupp's cast steel as used for guns, | 5000 kilos. per sq. c.m. or 72,258 lbs. per sq. inch, ..... | 1000 kilos. per sq. c.m. or 14,450 lbs. per sq. inch, ..... | 11·0 |
| Ordnance bronze, | 2200 kilos. per sq. c.m. or 31,792 lbs. per sq. inch, ..... | 385 kilos. per sq. c.m. or 5562 lbs. per sq. inch, ..... | 15·0 |

It was formerly believed, and this opinion has been verified by the Berlin experiments, that both steel and iron, after being repeatedly subjected to traction, torsion, or flexion, inferior to their supposed absolute power of resistance, at last break, even at a much less strain than is due to them, most probably owing to a change of their molecular structure. These experiments have shown that the number of strains of tension, deflection, and torsion, that a metal can bear, is in the inverse ratio of the amount of force to which they have been subjected. Professor Spangenberg found that a bar of phosphor bronze offered an immense resistance to torsion. A bar resisted without rupture—

| | Tons per sq. inch. |
|---|---|
| 3,871,500 bends right and left at a strain of | 14 |
| 1,996,900 " " " | 15 |
| 1,590,000 " " " | 16 |

Total, 7,458,400 bends to the right, and the same to the left.

Phosphor bronze alloys containing small percentages of phosphorus and tin are very malleable; they acquire by hammering, rolling, or drawing, great strength, toughness, and elasticity.

It was desirable to ascertain the resistance of the alloy to the chemical action of dilute sulphuric acid. For this purpose, on the 22nd of last April two similar sheets of copper and phosphor bronze were immersed in acid water of 10° Baumé strength, and at the temperature of the surrounding atmosphere. On the 28th of July it was found that the copper had lost 4·15 per cent., and the phosphor bronze only 2·3 per cent.

Phosphor brouze has been tested by Dr. Künzel as to its power of resisting the action of sea water. In a comparative experiment made at Blankenberghe, lasting over a period of six months, between the best English copper and phosphor bronze, the following results were arrived at:—

| Thickness of the Sheets = 0·236 Inches. | Weight before Immersion in Lbs. | Weight after Immersion in Lbs. | Loss of Weight. | |
|---|---|---|---|---|
| | | | In Lbs | PerCent. |
| Sheet of copper,.. | 74·4 | 72·2 | 2·2 | 3·015 |
| Ditto ditto, .. | 88·9 | 86·2 | 2·7 | 3·100 |
| Sheet of phosphor bronze,.. | 69·5 | 68·75 | 0·75 | 1·123 |
| Sheet of phosphor bronze,.. | 114·3 | 112·97 | 1·33 | 1·195 |

The loss in weight, therefore, due to the oxidizing action of sea water during the six months' trial, averaged for the English copper 3·058 per cent., while that of the phosphor bronze was but 1·158 per cent.

Several governments have experimented on the use of the alloy for making cannons. Without any exception, the result showed a much greater resisting power over that possessed by ordinary bronze. The following instances of the results arrived at will be of general interest.

In Belgium the ordinary bronze gun burst at the second shot, with a charge of 1 kilo. 250 grms. ($2\frac{3}{4}$ lbs.) of powder, and a cylindrical projectile weighing 8 kilos. 518 grms. ($18\frac{3}{4}$ lbs.). The phosphor bronze gun supported this charge perfectly; the normal charge was 500 grms. ($1\frac{1}{10}$th lb.) of powder, and 3 kilos. ($6\frac{3}{4}$ lbs.) of projectile.

* The composition of the alloy was in each case the same, but the mode of preparation was modified.

In France the ordinary bronze gun burst at the second shot, with a charge of 1 kilo. 500 grms. (3½ lbs.) of powder, and 16 kilos. (35¼ lbs.) of projectile, while the phosphor bronze gun was fired five times with this charge, and burst at the second shot with 1 kilo. 750 grams. (3⅞ lbs.) of powder, and a projectile of 20 kilos. (44 lbs.), owing to the wedging of this in the barrel. The normal charge was 550 grms. (1⅜ lb.) powder and a bomb of 4 kilos. (8¾ lbs.)

In Prussia it was shown in firing with the regulation charges, and diminishing, at each 50 shots, the exterior diameter of the chamber, that the phosphor bronze cannons only changed their dimensions when the thickness of the metal was below that of the dimensions of a cannon of the same calibre made of steel.

The Belgian government has adopted the phosphor bronze for small arms and for the harness buckles of all the cavalry.

Very satisfactory results were obtained by Major Majendie when testing phosphor bronze as to its liability to emit sparks when subjected to friction. The experiments were carried out in one of the workshops of the royal gunpowder mills at Waltham Abbey. A grindstone of 9 inches diameter was made to revolve very rapidly, so that any point on the grinding face would describe a distance of 2000 feet per minute; the metal was then pressed against the revolving stone, and the results proved that the harder descriptions of phosphor-bronze emit sparks less readily than the softer examples, and much less readily than ordinary gun metal or copper.

Dr. C. Künzel found as the results of experiments which he made on effects of friction between various substances, that the heat produced, other conditions being equal, is in proportion to the hardness of the substances; and, on the other hand, the greater the difference in the hardness of two substances rubbing against each other, the less the heat produced by the friction, and that the harder of the two heats more than the other. If friction take place between glass and cork the amount of heat received by the two respectively is as seven to one, and between bronze and cork, four to one.

For durability alone, of course, bearings should be of metal as hard as that of the arbors which they support, but considering the wear of the latter the former should be as soft as possible. In practice, however, certain precautions are to be observed; the bearing must not cut the arbor, and it must wear as little as possible; it should not get hot even when lubrication fails; and, lastly, it should possess resistance enough to bear all the shocks that fall upon it without being deformed or broken. The alloys of copper and tin generally in use are rarely homogeneous, with the exception of that which contains 82 to 83 parts of copper to 17 or 18 of tin. When there is less tin in the composition segregation takes place during cooling, which alters the homogeneousness of the alloy, and causes the cutting both of bearing and arbor. When an alloy of copper and tin sets slowly the first part consolidated is a very soft alloy, not containing more than 7 to 10 per cent. of tin; this forms, as it were, the shell of the bearing, while the hard alloy, containing 17 to 18 parts of tin, sets afterwards and fills up the pores of the shell. When a bearing thus formed is in work the soft alloy soon gives way, and the hard grains within attack the arbor, and are often torn out and carried away when grease fails.

A good bearing should be the opposite of the above. Its shell should be hard and durable, and the interior filled up with a softer composition. This result is obtained by fusing a certain proportion of phosphor bronze together with another alloy of different degree of fusibility, so as to produce by cooling two given alloys. The shell is then almost entirely formed of very tough and hard phosphor bronze, and the interior of the aforesaid soft alloy. The bearing may then be considered to consist of a series of layers of soft metal, enclosed in a casing of metal almost as hard as the arbor itself. The microscope reveals this disposition very plainly, and if one of these bearings be carefully submitted to heat, so as to cause the soft metal to run off, the rest will remain in the form of a spongy mass.

The following table shows the results obtained with various axle bearings:—

| Kind of Bearing. | Composition in 100 parts Alloy. | Comparative cost of 100 Kilos. Bearings, inclusive of Melting Expenses, Loss, &c. | 1 Kilo. Bearing Metal Runs. | | | Cost of Bearing Metal per Waggon with 4 Bearings per 100 Kilometres. | Names of Railroads where Used. |
|---|---|---|---|---|---|---|---|
| | | | German Miles. | Kilometres. | Wear per 100 Kilometres for 4 Bearings. | | |
| | | Marks. | | | Grammes. | S. Gr. | |
| Gun Metal,..... | 83 copper, 17 tin,..... | $260\frac{2}{10}$ | 12,052 | 90,390 | $11\frac{60}{100}$ | 0·301 | Austrian Railway. |
| " ..... | 82 copper, 18 tin,..... | $260\frac{8}{10}$ | 13,320 | 99,900 | $10\frac{1}{100}$ | 0·260 | Grand Central Belge. |
| White Metal,. .... | 3 copper, 90 tin, 7 antimony, | $298\frac{68}{100}$ | 9,104 | 78,280 | $14\frac{64}{100}$ | 0·395 | Austrian Railway. |
| " ..... | 5 copper, 85 tin, 10 antimony, | $293\frac{40}{100}$ | 11,750 | 88,145 | $11\frac{35}{100}$ | 0·331 | Niederschlesisch-Märkische Bahn |
| Phosphor bronze,.. | ..... | 350 | 57,226 | 429,200 | $2\frac{33}{100}$ | 0·081 | Grand Central Belge. |

The engines of H.M.S. *Shah* failed to act satisfactorily while the crank bearings were composed of white metal, since these became so hot under the enormous strain and friction that the metal underwent partial fusion. Hence it was impossible to drive the vessel at the requisite rate through the water, and so far this otherwise splendid frigate was a practical failure. But phosphor bronze having

been lately substituted for the brass and white metal, the bearings no longer run, although they may suffer some abrasion; and under the altered circumstances the *Shah* has attained her expected speed.

Bell-metal.—The standard composition of bells is about 78 of copper and 22 parts of tin, the latter being sometimes increased to compensate for the loss by oxidation. Generally, however, the founder takes—

| | |
|---|---|
| Copper, | 77 |
| Tin, | 21 |
| Antimony, | 2 |
| | 100 |

Such is the composition of *cymbals* and *tam-tams*, the specific gravity of which is 8·815. Admixture of other metals, such as lead and zinc, tend to injure the quality of the tone; still, as by their use the manufacture becomes less expensive, it is customary to employ them.

The following analysis of English bell-metal by Thomson shows the composition:—

| | |
|---|---|
| Copper, | 80·0 |
| Tin, | 10·1 |
| Zinc, | 5·6 |
| Lead, | 4·3 |
| | 100·0 |

Bells constituted of an alloy into which 20 to 22 per cent. of tin enter, are better and more sonorous than such as have the above composition. Besides the lead and zinc, a quantity of antimony and bismuth are sometimes introduced, in order to give a more crystalline grain to the metal, but also with the view of communicating a certain tone to the bells.

A certain requisite of bell-metal is ready fusibility, to communicate which the addition of some metals, such as those just mentioned, is made. It rarely happens that new materials are entirely used in preparing the bell-metal; old brasses and tins are worked in large quantities. The composition of these should, however, be known, so that the mean of the alloy may be such as will yield a bell of the required quality.

The moulds in which the metal is cast are constructed in much the same way as those of cannon, and the furnace employed for the fusion has also the same form, the temperature required, however, is less elevated. In the preparation of the alloy, the whole of the tin is not put in at the beginning, about one-third being reserved for addition when the whole of the bath is in perfect fusion. About one-tenth more than the weight which is destined for the bell should be submitted to the furnace, this quantity being expended in waste and scorification during the process. The tongue or clapper of the bell is usually of iron, suspended in the line of the centre of gravity, from a ring in the head, by a thong of horse leather or an iron rod. Its length ought to be such that when swung it will strike the bell near the verge, as then the sound produced is much greater than if the concussion took place further up.

The bells of clocks and those in domestic use have a somewhat larger proportion of zinc, the amount of tin being to the same extent lessened.

Estimation of Copper in Alloys.—For the sake of conciseness, it may be supposed that the alloy contains copper, zinc, nickel, tin, and lead, in order to prevent a repetition of the course to be pursued. About 30 grains of the alloy in filings, or else cut into thin slips, are introduced into a glass flask, and treated with concentrated nitric acid till the whole of the metal is decomposed. Some difficulty will attend this, unless the alloy is finely divided before subjecting it to the acid. When the whole has been oxidized, the excess of acid is to be expelled by evaporation, taking care that nothing be lost by spirting. Water must be added in sufficient abundance to dissolve the nitrates of copper, zinc, nickel, and lead from the insoluble stannic acid. Heat is applied, and after the copper is dissolved the remaining precipitate is thrown upon a filter, washed well with water to remove all traces of the accompanying salts, and afterwards dried in the water bath, ignited in the usual manner, and weighed. The filtrate from the tin, containing the nitrates of lead, zinc, nickel, and copper, is treated with sulphuric acid in excess, and evaporated till the liquid is concentrated. Sulphate of lead is thus precipitated, which must be collected upon a filter, washed, dried, ignited, and weighed. In the liquid filtered from the sulphate of lead, a precipitate of sulphide of copper is thrown down by transmitting a current of sulphuretted hydrogen through it. This precipitate is filtered and washed thoroughly, then dissolved in hot weak nitric acid and boiled to expel all traces of the gas, and then filtered. The nitrate of copper solution is precipitated by potassium hydrate, taking care that the liquor be previously diluted and raised nearly to the boiling point at the time of pouring in the alkali. The whole is further heated till the oxide of copper falls in the form of a dense black powder. This, which is the anhydrous protoxide, is filtered, and subjected to a prolonged washing with boiling distilled water, to separate the last traces of potassa. When thoroughly purified it is dried, ignited, and weighed.

The solution from the potassium sulphide is boiled to dispel all traces of the gas. Carbonate of soda is added, and a precipitate of carbonate of nickel and carbonate of zinc falls. This is collected, washed, and subsequently dissolved in hydrochloric acid, the solution evaporated, potassium hydrate added in excess, and after this hydrocyanic acid, till the precipitate which was determined is redissolved. Finally, potassium sulphide is added to this liquor to precipitate the zinc in the form of white sulphide. After removing the latter compound and washing it thoroughly, the filtrate and washings are treated with aqua regia and evaporated, to decompose the nickel potassium cyanide. Finally, by adding potassium hydrate oxide of nickel is precipitated, and after washing, drying, and igniting, is weighed.

Other courses may be pursued in the analyses of the compound metal above mentioned, but that just described will answer in general most of the purposes of the manufacturer.

*Volumetric Method of Assaying Brass, Bronze, &c.*—

This process, devised by E. O. Brown (Chemical Department, Woolwich Arsenal), is exceedingly accurate. 10 grains of copper are dissolved in dilute nitric acid, and the solution boiled until free from nitrous acid; it is then diluted with about an ounce of water, and carbonate of soda added until a portion of the copper is precipitated. Pure acetic acid is then added in excess, and the solution poured into a flask capable of holding about 12 ounces. About 60 grains of iodide of potassium are then thrown into the flask, and sufficient time having been allowed for the crystals to dissolve, a standard solution of hyposulphite of soda (sodium thiosulphate, $Na_2S_2O_3$) is added until the greater part of the iodine has disappeared, which is indicated by the liquid changing from a brown to a yellow colour. A clear solution of starch is then added, and the addition of the hyposulphite of soda cautiously continued until no further effect is produced. The bleaching effected by the last portions of hyposulphite of soda may be best seen by allowing the drops to fall into the centre of the flask whilst the liquid is in motion, when streaks of a lighter colour will be produced, so long as any iodine remains. The quantity of iodine employed must be at least six times the weight of the copper to be determined, and it must be free from potassium iodate. The acetic acid must contain no sulphurous acid.

The solution of starch should be made by boiling with a large quantity of water, any undissolved portions allowed to subside, and the clear liquid only used.

The solution of hyposulphite of soda is obtained by dissolving 4000 grains of the salt in 2 gallons of water. It is standardized by means of electrotyped copper by the above process.

*Coloration Test.*—The following process is given by Ure for the determination of small quantities of copper. This method depends on the fact that the intensity of the blue colour of an ammoniacal solution of copper is proportionate to the quantity of copper present.

1. A standard coloration test solution is prepared by dissolving a known weight of copper (0·5 or 1 grain) in dilute nitric acid, adding excess of ammonia, and diluting to 10,000 grains. This solution is kept in a well-stoppered, long, glass, graduated bottle. The ammoniacal solution of copper obtained by the decomposition of a given weight of the substance, is transferred to a graduated measure of the same shape and capacity, and water added until the tint corresponds to that of the standard coloration test. The percentage of copper is calculated as follows:—10,000 grains of the standard coloration test contains 0·5 grain copper; the solution of 100 grains of the substance required dilution to 8000 grains.

10,000 : 8000 : : 0·5 : 0·4 per cent. of copper.

2. The adaptation of this method, generally adopted in smelting works for testing slags, is as follows:—A series of standard coloration test solutions of copper are prepared and kept in a number of colourless square or round glass bottles, of exactly the same shape and capacity. If the series comprises ten bottles, the first bottle may contain $\frac{1}{10}$th of a grain of copper, the second $\frac{2}{10}$ths, and so on to the last, of 1 grain. From 50 to 100 grains of the powdered slag or other substance are treated with nitric or nitro-hydrochloric acid until decomposition is effected. In some cases previous fusion with carbonate of soda may be necessary. The solution is diluted with water, excess of ammonia added, and filtered, or the precipitate allowed to settle, and the solution decanted. If necessary, the precipitate obtained by ammonia is redissolved in acid and re-precipitated by ammonia; and if the filtrate has a blue tint, it must be added to that previously obtained. The whole of the solution is then diluted with water until there is the same volume of solution as in one of the test bottles. The colour is then compared with the coloration test bottles, and the one it corresponds to represents the amount of copper present in the quantity of substance operated on. From this datum the percentage of copper is calculated. A more rapid mode of operating is to make up the whole body of the ammoniacal solution containing the precipitate to a known volume, which is a multiple of the amount in the test bottles, and after the precipitate has settled to take a fractional part of this in a bottle of precisely the size and shape of the test bottles.

If nickel or cobalt be present the copper must first be separated by means of sulphuretted hydrogen or otherwise, and the precipitate redissolved in acid.

COPPER SALTS.—The only compounds of copper which have been prepared to any great commercial value are the acetate, sulphate, and carbonate.

Oxide of copper, CuO, chemically termed copper monoxide, cupric oxide, or black oxide of copper, has been employed to some extent as a pigment, and is known as powder blue. It is, however, an unstable colour, and consequently not much used. It may be prepared in various ways in the laboratory. If thin plates of copper be heated to low redness in the air, their surfaces become readily tarnished; a yellow colour, changing to a violet, is produced, owing to the formation of oxide of copper. Should the heat be continued and increased to redness, and then slackened, a coating of oxide of copper will be thrown off in the form of black scales. The same substance is obtained by heating nitrate of copper to redness in a crucible, nitrous acid and oxygen being evolved. Thus obtained, it is useless for the requirements of art in consequence of its colour, which is black or brownish-black. In this state it is powerfully hygroscopic, attracting moisture from the air with avidity. It requires the highest temperature of a wind furnace to fuse it, and then it parts with a certain proportion of oxygen, becoming a suboxide of the metal. Hydrogen passed over it at a red heat effects a rapid reduction, and metal results. The same change occurs when it is heated with organic substances in close vessels. When fused with vitreous matters, such as glass, it dissolves, and communicates to the mass a blue tint resembling that produced by oxide of cobalt. It

was thus that the ancients, long before cobalt was known, prepared glass of a fine azure tint. The specific gravity of the black oxide of copper is 6·4. Most acids dissolve it, forming more or less blue solutions, from which potassium hydrate precipitates a bluish hydrate. Heated to the boiling point it is converted into a dark-brown powder, which is anhydrous cupric oxide, this hydrate being decomposed by heat even in presence of water. Ammonia, sparingly added, likewise throws down a similar compound, which dissolves in an excess of the reagent, forming a beautiful violet-coloured fluid. The carbonates of the fixed alkalies occasion precipitates in solution of oxide of copper; but the most characteristic is the peculiar reddish-brown which it yields with ferrocyanide of potassium. Its chemical symbol is CuO, and its atomic or equivalent weight, 79·4.

When the oxide of copper is precipitated from its solutions by potassium hydrate, it forms a blue compound of $Cu_2H_2O_2$ or $CuO.H_2O$, which is used as a pigment, more especially by paper-stainers. DUMAS gives the following directions for its preparation:—Dissolve 6 parts of sulphate of copper and 3 parts of chloride of calcium, separately, in water; then mix both liquids, and after the sulphate of lime falls to the bottom, decant the liquid chloride of copper into a third vessel, where it must be well agitated with a cream made of 1½ part of lime. A greenish precipitate, consisting of a basic chloride of copper, falls, which is the crude compound sought. After collecting and washing thoroughly, it is ground with one-fourth part each of hydrate of lime and pearl ash, and put into bottles. It is customary to add a quarter of a part of chloride of ammonium, and half a part of sulphate of copper, when packing, to enable it to retain its blue colour. If left exposed, the bluish tint would disappear, and a green be substituted. Indeed, the hue changes to this, after being applied for some time, so that it is not used to any great extent.

When 5 parts of black oxide of copper and 4 parts of copper filings are heated together in a closed crucible, cuprous oxide ($Cu_2O$, red oxide or suboxide of copper) is formed. It is used in the glass-house to stain glass red. The colour produced is very rich.

All compounds of copper are poisonous. In some cases PEREIRA says that small doses of salts of copper give relief in diseases of the nervous system, and for this purpose have been administered under the title of *tonics*, *antispasmodics*, or *alteratives*, according to the nature of the malady: but when taken in larger quantities they occasion gastro-intestinal inflammation, and disorder the functions of the nervous system. When death ensues from these causes it is said to be produced by *acute poisoning by copper*, the symptoms of which are a cupreous taste, violent vomiting, griping pains, cramps in the legs and thighs, headache, giddiness, convulsions, and insensibility. The usual antidote for cupreous poisons is albumen or white of egg; but gluten or milk in large quantities will serve the same end. An insoluble albuminous compound of cupric oxide is formed, which must, however, be removed from the stomach immediately, otherwise the poison will ultimately, if in sufficient quantity, prove fatal.

Preparations of copper have been topically applied with considerable benefit to the patient. They act as caustics, irritants, and astringents.

Among the salts of copper the carbonate and sulphate are the only ones of which a description will be given here. For Acetate of Copper see ACETIC ACID.

CARBONATE OF COPPER.—This salt, under the title of *verditer*, is employed in considerable quantities as a pigment. The composition is not, however, a true carbonate, but a mixture of this and oxide of copper. The mineral azurite, when powdered, gives a very fine blue colour; but it is costly.

Verditer is prepared from metallic copper and its sulphate by the following process:—About 222 lbs. of copper are mixed intimately, under edge stones, with about an equal weight of common salt, the powder being afterwards made into a paste with water. 225 lbs. of thin sheet copper, cut into pieces 1 inch square, are agitated in a wooden tank or vessel with 2 or 3 lbs. of strong sulphuric acid, diluted with water, to remove any coatings of oxide or other impurities which might prevent the oxidation of the metal in a subsequent operation. As soon as the acid has acted sufficiently upon the surface it is decanted, and the fragments introduced into barrels, which are made to rotate on their axes, and thoroughly washed with water. Afterwards the bits of metal are mixed with the saline paste already mentioned, and deposited in layers in the bottom of what is called the oxidation chest. Here the metal, through the agency of the salts which absorb oxygen, becomes oxidized in proportion to the extent of surface in contact with the air. In order, therefore, that the transformation may be as perfect as possible, the layers should not be over thick; and they ought to be turned over once a week to present a fresh surface to the atmosphere. This is done by turning the contents of the chest into an empty one, and transferring the matter back into the former again. At the close of three months the process of oxidation comes to an end. The mass is now turned over, and particles of metal which might still remain are carefully picked out. The residue is washed with the smallest quantity of water to separate the saline matter, and then filtered. The magma (*schlam*) remaining on the filter is next transferred in buckets which hold about 30 lbs. into a large tub, and for every 6 measures introduced 12 lbs. of hydrochloric acid, of specific gravity 1·109, are added. The whole is then well commingled and left at rest for thirty-six or forty-eight hours. The effect of this is to produce a soluble chloride of copper, from which the oxide is to be thrown down afterwards by a solution of an alkali. This is prepared in the usual way with caustic lime, and the proportion used is 15 measures—specific gravity being 1·142—to every 6 pailfuls of the acidified precipitate already mentioned. After the usual time for standing has elapsed the mixture is transferred quickly

into the tank containing the alkali, and the whole briskly stirred till it becomes rather consistent, when it is left to repose for thirty-six to forty-eight hours. The precipitate by this time will have subsided. The supernatant fluid is siphoned, and the blue precipitate repeatedly washed with water, and, after the settling of the solid matter, decanted.

When all traces of alkalinity have been removed the precipitate is thrown into filter-bags, where it is freely exposed and repeatedly moistened, and finally allowed to drain. After this the matter is cut into small pieces and exposed to spontaneous dessication in the air till it becomes thoroughly dry. The latter may be conducted in a chamber, but the temperature should not exceed 78° Fahr.

If the several operations be properly conducted, and the final exsiccation thoroughly performed, a beautiful product results; but the smallest amount of moisture, if retained, tends to injure the colour, on which the value of the substance almost entirely depends.

Another variety of the same may be obtained by agitating chalk with a solution of nitrate of copper for some time; double decomposition takes place, and carbonate of copper precipitates. When it has completely subsided the solution of nitrate of lime is decanted, and fresh additions of water made after each decantation till the residue is sufficiently purified. The colour of the precipitate when dried is greenish, but the blue shade is communicated by mixing with it 8 or 10 per cent. of fresh-burnt lime. If this addition be made while the compound is in the pasty state, and the whole well triturated for some time, a uniform hue is produced.

An inferior kind of verditer is prepared by mixing subsulphate of copper and chalk together, and washing as above described.

The composition of this body varies with the nature of the course followed in its manufacture; but a good article approaches to the annexed results of the analyses of samples of verditer:—

| | Theory. | Berzelius. | Proust. |
|---|---|---|---|
| Oxide of copper,..... | 72·07 | .. 71·70 | .. 69·5 |
| Carbonic acid,..... | 19·82 | .. 19·73 | .. 25·0 |
| Water,..... | 8·11 | .. 8·57 | .. 5·5 |
| | 100·00 | 100·00 | 100·0 |

Verditer is employed to a large extent in the manufacture of paints, and as a substitute for verdigris.

Sulphate of Copper.—*Roman vitriol*, *Blue vitriol*, *Blue stone*, *Cupric sulphate* ($CuSO_4.5H_2O$).—This is the most important of the salts of copper, and the one which is manufactured in largest quantities. Many ways are known for preparing it in the laboratory—such as exposing pure copper in thin sheets to the joint action of dilute sulphuric acid and air; treating freshly precipitated oxide of copper with diluted sulphuric acid, or boiling the metal with either concentrated sulphuric acid, or the acid diluted with an equal bulk of water. In all three a solution of sulphate of copper is obtained, from which the salt may be removed in well-defined rhomboidal crystals of a fine sapphire blue colour. They are liable to effloresce when exposed to the air, owing to the escape of water of crystallization. Four parts of cold and two parts of boiling water are required for their solution. In crystallizing, sulphate of copper takes up five equivalents of water, of which four may be expelled at 212° Fahr., but the expulsion of the last requires a temperature of 400° Fahr. Deprived of moisture, the salt is white; in this state, on account of its hygroscopic properties, it is employed as a test for determining the presence of water in some spirituous liquids, such as alcohol, &c.; when exposed to moist air, or to contact with aqueous liquids, it re-assumes its usual bluish colour. At a very high temperature sulphuric together with sulphurous acid and oxygen are expelled, and cupric oxide is left. When heated in close vessels with an excess of charcoal, reduction takes place, sulphurous and carbonic acids are evolved, and metallic copper remains. Sulphate of copper is decomposed by hydrochloric acid, chloride of copper being formed and sulphuric acid set free. Anhydrous sulphate of copper is represented as $CuSO_4$.

Besides the above methods, many others are followed. Already, when describing the manufacture of copper from its ores, occasion has offered of showing that, by calcining the pyritous minerals in contact with air, the sulphur and copper are oxidized, so as to give rise to a sulphate of the metal; this is more especially the case if nitrate, or any other oxidizing substance, be heated with the mineral, for then nearly the whole of the sulphur will be converted into sulphuric acid, which unites itself with the oxide and forms the substance. For extracting it, the roasted ore is thrown into a tank, and a moderate amount of water added, and left to digest for some time, during which those portions of the ore that were unaffected in the furnace now undergo oxidation, and produce sulphate of copper. The liquor after being drawn off is evaporated to the crystallizing point, and the residue left in the first tank, if not entirely exhausted of its copper, is subjected to a second roasting with a fresh quantity of ore, and exhausted with water as in the preceding instance.

A very small proportion only of the sulphate of copper manufactured is obtained by the above process, the chief bulk being prepared by acting upon the scales which are separated from the metal when undergoing the process of lamination; the dipping liquor of the coppersmith is also used for the same purpose. The details of the manufacture are very simple:—A stout wooden vessel lined with lead is provided, and into this a certain quantity of copper scales and strong sulphuric acid is introduced: both are agitated, and the whole left till the solution becomes saturated with the sulphate of copper. To assist the action of the acid, steam is blown through a lead pipe passing nearly to the bottom of the tank. When the acid becomes saturated, the liquor is drawn off into other leaden vessels, arranged in a warm room, and allowed to crystallize. In the course of five or six days a crop will be obtained; the mother-lye is decanted and added to fresh liquor

that is ready for crystallization. After draining, the crystals are dried and packed for sale; sometimes they are packed when merely drained of their moisture. In this operation all the scales are not dissolved—only such portions as have undergone thorough oxidation. The residuary matter remaining in the tank after the action of the acid has ceased is washed with water, dried, and sent to the furnace with blister copper to be refined.

The following examples will serve to illustrate the process on the large scale. 5 cwts. 2 qrs. by weight of copper scales were treated with 685 lbs. of sulphuric acid of 1·700 density, water being added in sufficient quantity, and the produce was 5 cwts. 2 qrs. 24 lbs. of crystals of sulphate, together with 122 galls. of mother-liquor of 1·180 spec. grav., and 160 galls. of 1·100 density. By operating upon a portion of those liquors, it was found that the total weight of the sulphate of copper produced was equal to 1240 lbs., and that for their production only 350 lbs. of the scales were taken up.

In another instance, 7 cwts. of the scales were taken, and 800 lbs. of strong sulphuric acid of specific gravity 1·700 added to them, together with a sufficient quantity of water; 7 cwts. 1 qr. 14 lbs. weight of crystallized sulphate of copper were obtained, together with 138 galls. of mother-liquor of a specific gravity of 1·176, and 116 galls. of 1·080 gravity, both together holding 825 lbs. of the salt in solution, so that the total quantity was 1651 lbs. of salt, leaving 2 cwts. 3 qrs. 18 lbs. of the scales unacted upon.

The dipping liquor of the brazier is also used as a source of sulphate of copper; but the product which it affords is not of good quality, owing to brasses and other alloys being subjected to the action of the acid, and of course sulphates of zinc, iron, and other bases being present as impurities. Occasionally, this *pickle* is added to the cupreous liquor obtained by acting upon the scales with vitriol, and the whole crystallized; the product, although serviceable in some cases, cannot, however, be used in place of pure salt.

Considerable quantities of sulphate of copper are employed in the preparation of other compounds, such as verditer, acetate of copper, *Scheele's green*, &c. It has likewise been found serviceable in agriculture for the purpose of steeping the seeds, in order, as is said, to prevent thereby the ravages of insects, the smut and other analogous blights in the crop; but the inferior kinds are taken for this purpose. It has also been employed to saturate wood or timber as a preventive against the dry rot. It is also very largely employed as a base for several of the green and blue colours applied in calico printing.

The method of analysis which is followed in determining the value of the salts of copper is similar to that described for the estimation of copper in ores or alloys of the metal.

The sulphate of copper of commerce is often contaminated with sulphate of iron, zinc, or magnesium.

If the presence of iron alone be suspected, dissolve the crystals in water, boil for some time with nitric acid, and then add excess of ammonia. The ammonia precipitates at first both the iron and the copper, but the latter speedily redissolves, whilst the ferric oxide is left as insoluble reddish brown flakes.

If the sulphates of zinc and magnesium are likewise present, dissolve a weighed quantity of the salt in water, acidify strongly with hydrochloric acid, and pass a current of sulphuretted hydrogen slowly through the acid solution until it smells strongly of the gas. A black precipitate of copper sulphide is produced; filter rapidly, and wash with sulphuretted hydrogen water. The sulphide of copper is then dried, and treated in a beaker with nitric acid until the sulphur is separated. The solution is then filtered, and the cupric oxide precipitated with potassium hydrate; after boiling the precipitate is collected, dried, and ignited.

The liquor filtered from the sulphide of copper is heated till all smell of sulphuretted hydrogen ceases, nitric acid is then poured on it, and the whole boiled to convert the iron into ferric oxide; the acid liquor is then neutralized with ammonia, and precipitated by succinate of ammonium. The liquor filtered off is then heated with ammonium sulphide, which, if zinc be present, will produce white precipitate. The liquor from the zinc sulphide is then supersaturated with hydrochloric acid to decompose the ammonium sulphide, and the magnesia, if any, precipitated as bibasic phosphate of ammonium and magnesium by means of a solution of sodium phosphate and ammonia.

**DISINFECTANTS.**—*Desinfectants*, French; *desinficirungs - mittels*, German; *disinfettanti*, Italian.—The word "disinfectant," in its full and general sense, means a substance that will remove, neutralise, or destroy that which is noxious to animal life. Antiseptics, or those substances which prevent the organic matter with which they are placed in contact from entering into a state of putrefaction, are also to that extent disinfectants. The burning of bedding, &c., when its object is to destroy contagion, is disinfection, since the hurtful organic matter is thus destroyed by fire.

Disinfectants may be divided into—volatile, in the form of gas or vapour; and solid or liquid.

*Volatile Disinfectants.*—1. Substances which, like the halogens, appear to form substitution compounds—*e.g.*, chlorine, bromine, iodine.

2. Substances which probably combine chemically, and thus destroy contagion:—Sulphurous acid, nitrous acid, fumes of other acids.

3. Oxidizing substances, such as pure air, oxygen, ozone.

4. The volatile oils, &c., feeble disinfectants, supposed, however, to oxidize—Camphor, the oil of hops, rue, rosemary, chamomile, &c.

*Liquid and Solid Disinfectants and Disinfecting Agencies.*—1. All soluble chlorides, particularly those of the alkaline metals:—Calcium, iron, copper, manganese, zinc, aluminium, mercury, &c.

2. All soluble sulphates, especially sulphates of iron and aluminium.

3. All soluble sulphites.

4. Some acetates, as acetate of iron.

5. Some nitrates, as nitrates of potassium and sodium.

6. Certain agents which appear to arrest putrefaction, or condense certain gases without either destruction or oxidation:—Carbolic acid, salicylic acid, tar acids, charcoal, great cold, heat sufficient to dry organic substances, but not to char them.

7. Preservative liquids and solutions. Many of these act by coagulating the albumen of organized bodies. Antiseptics, alcohol, solutions of corrosive sublimate, common salt, and saltpetre.

8. Destructive agents. Not true disinfectants; they act not by disinfection, but by destruction:—A dry heat of 200° to 400° Fahr.; strong acids and strong alkaline solutions.

9. Agents which act in many ways, partly by absorbing moisture, partly by condensing gases, and partly by a peculiar action on organic matter analogous to tanning. These are:—Dry earths, clays, and the natural and artificial compounds of aluminium. —(Blyth. *Dict. of Hygiène*).

The ancients seem to have attained the knowledge of antiseptics at a very early period—their first attention being directed to the disposal of the dead in such a fashion that the body should cease to be hurtful or annoying to the living. This was doubtless the primary idea of disinfection. In embalming the body, after the removal of the viscera, was washed with palm oil and aromatic substances, and was then filled up with powdered myrrh, cassia, and other perfumes; after this it was buried in *natron* (soda) for seventy days, and, finally, was protected from atmospheric action by being enveloped in gummed cloth. Or, for a cheaper process, the intestines were filled with what Herodotus termed *cedar oil* (turpentine) and the body salted; the former having consumed the flesh, leaving only the skin and bones, was then removed. At other times, it is stated, the corpse was merely treated with a cleansing wash, and then *steeped* in soda. Others, and the greater part of the Egyptian mummies, were treated with asphalt only, converting the body into one black mass.

The burning of bodies was another mode of disposing of animal matter liable to decomposition. The ashes were generally deposited in urns; hence the little niches like pigeon-holes, forming the *columbaria* of the Romans, for the reception of such vessels.

As organic substances which are deprived of their water do not decompose, drying was also adopted at an early period, both amongst the Egyptians and in other countries, as a means of stopping eremacausis, *i.e.*, the slow oxidation of organized structures; and there can be little doubt that this formed a part of every process of embalming. The preservation of these bodies is due to the dryness of the receptacles, as well as to the art of the embalmer.

Washing with pure water to remove all putrescent or putrescible matters has always been, and must continue to be, the most important disinfectant, whenever it can be applied. Hence came the purification of early times. This was undertaken whenever anything noisome, especially a dead body, had been touched. The Mosaic command on such occasions is to wash the clothes of the infected person, and set him apart as unclean until the morning, or longer according to circumstances; thus ablution is considered insufficient—time also is needed. This is not a mere symbolical or moral impurity demanding time, even after the cleansing, without a physical cause; it is also a kind of quarantine, established in private, perhaps useful, and at least incapable of doing injury. The disinfection of houses was the work of the Jewish priests.

The soil is a very valuable disinfectant, decomposing animal matter with great rapidity, the gases given off being, when sufficient space has been allowed for the remains, absolutely innocuous.

Efficacious as the soil is for the absorption and gradual destruction of bodies buried in it, it has been found in large towns that the amount of soil covering the dead has been insufficient; most nations, therefore, have interred their dead in the suburbs and less populous localities.

During the last few years the process of burning the dead has been advocated, and cremation has been carried out, though on a very limited scale, in some continental towns—the dead body being placed in a furnace specially constructed for the purpose, and completely calcined and reduced to ashes.

Embalming has been resorted to in Europe from the very earliest times, and with great success. The remains of the French kings disinterred in St. Denis by the revolutionists preserved their countenances, it is said, perfectly when first uncovered; but immediately disintegrated when exposed to air. Abundant instances are found in history of similar preservation, although the particulars of the processes adopted in the middle ages are even less known than the Egyptian methods, while, at the same time, they appear to have been more successful. Sometimes the preservation is effected by the mere action of a constant current of air. This may be readily believed of a warm climate; but the same result occurs at Bonn, in the vault of a chapel, where the bodies of the monks are dried up and shrivelled, but not decomposed. No means whatever, it is said, are used to obtain this result, further than placing an open coffin containing the body in a dry repository through which the wind is continually blowing.

Out of the original idea of purification and disinfection many ceremonies have arisen; such, in all probability, are *lustrations*, and all those in which incense is used. When Ulysses burnt sulphur to remove the infection emanating from the dead bodies of the suitors, he retained the original rite, which had not lost its meaning in mere antics. When the Roman shepherds burnt sulphur and herbs once a year, sacrificing to Pales, and adorning their folds with wreaths, part of the original process of disinfection was retained, though it was rapidly degenerating into mummery. The perfumed oils put on

the bodies of the dead were more for the concealment of the effluvia than for any powerful disinfectant quality which they possessed.

Closely connected with the decomposition of animal matter is fermentation; and it has been of late years thoroughly established that bodies or circumstances which prevent the one interrupt the other. In the manufacture of wine, fermentation may be checked by the use of some oils, such as turpentine, as well as acids, especially carbolic, sulphurous, &c. When fermentation of grape juice is completed, oxidation and the formation of acetic acid commence, or complete decay sets in. To prevent this the ancients employed agents of various kinds—sea-water, turpentine or resins, caustic lime (either from common limestone, marble, or shells), gypsum, aromatic herbs and spices, gums, &c. The vessels were also sometimes lined with pitch, and occasionally powdered pitch was thrown into the fermenting juices. Besides these were used almonds, raisins steeped in must, parched salt, goats' milk, cedar cones, gall-nuts, and blazing pine-torches, or red-hot irons quenched in the liquid. Salts of lead were also in request, either to alter the taste or to prevent decomposition, and remove impure matter and clarify the wine. In some places aloes were employed, producing a slight bitter, like that of the well-hopped Burton ale of the present day; in others the flavour—as in the Scotch and Irish whisky—was given by smoke.

Although the ancients do not appear to have had very accurate knowledge as to the conditions requisite for the decomposition of organic matter generally, they proved their knowledge of the necessity of preventing the emanations of marshes by drying them up; of shutting out certain winds, by completely stopping all the crevices on the exposed side of their houses; whilst they also fused aromatic herbs and kindled fires in the streets in time of plague.

Causes of Infection.—Infection arises from germinating matter, which, coming in contact with that which is healthy or sound, but contains the constituents necessary for carrying on its growth, induces a continuation of the decay.

Animal and vegetable matters were formerly supposed to decompose spontaneously; but it is now known that in no case can either putrefaction or infection occur without the presence of *living germs*.

Diseases may be propagated, be it granted, by contact with infected persons, but to one common source all must in the first instance be due, viz., to the presence of infectious matter, *i.e.*, matter capable of propagating disease.

There is much dispute as to the origin of various diseases, and also as to the nature and manner of their infection; in treating of disinfection we must only aim at what can be undoubtedly accomplished, viz., the method of preventing or destroying what is noxious or contagious rather than considering whether each distinct kind of decomposition and each specific form of infectious disease are the results of vital manifestation of special germs differing in each case, or whether they are caused by the molecular movements of organic matter in peculiar states of decay.

When a country is badly drained, and there is no outlet for the products of the decomposition of plants but the air, it often happens that disease spreads rapidly. If the land be properly drained, these emanations passing through the soil become disinfected, and a comparatively healthy atmosphere results. Marshes in all ages have been unwholesome; but they are so in proportion to the temperature and the state of vegetation. A damp climate and a moist soil, such as those of Holland, do not produce disease in an equal degree with a similar condition in the tropics, where decay is more accelerated.

Ponds, and such collections of water which are too shallow to prevent rapid decomposition, and allow the sun's rays to enter so as to encourage the growth of plants at the bottom, become fertile sources of disease. They can only be disinfected entirely by destruction of the vegetation.

Masses of matter in a state of decomposition around a dwelling may easily become centres of contagion; and the best method of dealing with these is to remove them immediately; but if in a dangerous condition, to disinfect them previously, as their removal without previous disinfection abundantly disseminates the noxious matter.

A still atmosphere induces the spread of infection, as a whole district or country may become like a closed vessel, rapidly filling up with impure matters, and pestilence being consequently generated. Hurricanes, it is well known, have a powerful tendency to stop the progress of disease (probably by chilling the germs and rendering them inactive).

Air is the great vehicle for conveying organic matter, and indeed it would be difficult to imagine a state of the atmosphere in which organic matter did not exist, and the recent researches of Dr. Angus Smith on air, collected in various rooms and crowded places, prove to us the immense importance of good ventilation. Even the air which has been breathed by healthy persons is found to be injurious if allowed to collect; but when emanating from those with unhealthy constitutions, it communicates disease very readily. Its first action is on the nasal organ, where its nature generally gives notice of contiguous evil; but when persons are accustomed to living in impure air, habit causes them to be insensible to its effects. It next enters the lungs, where the blood absorbs it; distemper is thereby communicated to the most vital parts in a direct manner.

*Dust and Germ Laden Air.*—In the year 1868 Professor Tyndall communicated to the Royal Society the results of his investigations on chemical reactions produced by light. In these researches the vapours of volatile liquids were subjected to the action of concentrated sunlight, or to the concentrated beam of the electric light.

The apparatus employed in these experiments consisted of an experimental glass tube, about 3 feet long and 3 inches in diameter. Its ends were stopped by plates of glass. The tube was connected with an air-pump and exhausted of air. Purified

air was then allowed to bubble slowly through a certain volatile liquid, contained in a flask, and when charged with the vapour of this liquid to pass into the experimental glass tube. A powerfully converged beam from the electric light was then passed into the tube, and the vapour therein contained being decomposed by the action of the beam, was precipitated in myriads of fine particles.

In all cases where the amount of vapour in the experimental tube was large, the decomposing action was very rapid, and the particles constituting the precipitated cloud were so large in size as to whiten the luminous beam. If, however, the vapour in the experimental tube was in a highly attenuated condition, the decomposing action of the beam was very slow, and the cloud particles when first precipitated were infinitesimal in size. Thus, purified air, charged with the vapour of the liquid nitrite of amyl, was passed into the exhausted experimental tube until it was completely filled. A convergent beam from the electric light was then sent into the tube. For a moment the tube was optically empty, nothing whatever was to be seen within it; but before a second had elapsed decomposition took place, and a dense cloud of particles almost instantaneously was precipitated upon the beam. So rapid and intense was this precipitation, that the convergent cone of light which a moment before was invisible flashed suddenly forth like a solid luminous spear. In an exceedingly short time the tube was filled with a dense cloud, which reflected brilliantly the luminous beam.

The experimental tube was then charged with the vapour of the liquid nitrite of amyl in a highly attenuated condition. The convergent beam of light was passed into the tube as before, but it required some minutes' exposure to the decomposing beam before the action became manifest. Decomposition then commenced, and advanced slowly, the cloud particles precipitated being almost infinitesimal in size. The cloud thus formed presented the most delicate appearance, and reflected a deep and rich blue light, equalling the finest blue of the sky.

In this manner a large number of vapours were submitted to the action of light and decomposed. Various gases were used instead of air as the vehicle for carrying the vapour, proving the decomposition to take place in the vapour alone, and not to any interaction between the vapour and its vehicle. The heat rays and the chemical rays were separated, and the vapour submitted to the action of each proved the power of decomposition to be due to the latter and not to the former. With a proper mixture of vapours in an attenuated condition, gorgeous blue clouds were produced, which exhibited all the phenomena of polarization obtainable from the light of the sky.

The ordinary air of the laboratory in which these investigations were conducted, although invisible in diffuse daylight, was found loaded with floating dust when illuminated by a powerful beam of light. During the early part of the investigation Professor Tyndall was much troubled by the appearance of this floating dust in his experimental tube. For no matter what precautions were taken as to its cleanliness, or with what care and slowness the vapour-laden air was admitted, these floating dust particles were invariably present, the condensed beam of light passed into the tube instantly revealing them.

It was of importance, therefore, especially when the decomposing action was slow and the precipitated cloud very delicate in texture, that the space containing the vapours should embrace no visible thing; that no substance capable of scattering the light in the slightest degree should at the outset be found in the experimental tube.

With a view to the removal of this floating matter from the air, the following series of experiments was made:—

Before the air entered the flask containing the liquid whose vapour was to be examined, it was thoroughly dried and its carbonic acid removed by passing it in succession through two tubes; one of them containing fragments of glass wetted with concentrated sulphuric acid, the other fragments of marble wetted with a strong solution of caustic potash. But although the acid will destroy all the floating matter of the air when left sufficiently long in contact with it, it is incompetent to do so when the air is carried over it, even with exceeding slowness. The aspect was substantially the same when the air was permitted to bubble through the liquid acid and through the solution of potash. The core of the bubble does not touch the acid, and even the dust particles which come into contact with the acid require time to be wetted by it.

Thus, successive charges of air were admitted through the potash and sulphuric acid into the exhausted experimental tube. Prior to the admission of air the tube was optically empty; it contained nothing competent to scatter the light. After the air had entered the tube the conical track of the electric beam was in all cases clearly revealed.

After trying the intereception of the floating matter in various ways, the air immediately before entering through the drying apparatus into the exhausted experimental tube was permitted to pass over the top of a spirit lamp flame. The floating matter no longer appeared, having been burnt up by the flame. It was therefore of organic origin, for if it had been inorganic it would have been incombustible.

In place of the drying apparatus a small platinum tube which could be heated to vivid redness was connected with the experimental tube. The tube also contained a roll of platinum gauze, which, while it permitted the air to pass through it, insured the practical contact of the dust with the incandescent metal. The air of the laboratory was permitted to enter the experimental tube, sometimes through the cold and sometimes through the heated tube of platinum. The rapidity of admission was also varied. In the first column of the following table the quantity of air operated on is expressed by the number of inches which the mercury gauge of the

air-pump sank when the air entered. In the second column the condition of the platinum tube is mentioned, and in the third the state of the air which entered the experimental tube.

| Quantity of Air. | State of Platinum Tube. | State of Experimental Tube. |
|---|---|---|
| 15 inches .. | Cold .. | Full of particles. |
| 15 " .. | Red-hot .. | Optically empty. |

The phrase "optically empty" shows that when the conditions of perfect combustion were present the floating matter totally disappeared. It was wholly burnt up, leaving no sensible residue. The experiment was repeated many times with the same invariable result.

In a cylindrical beam, which powerfully illuminated the dust of the laboratory, was placed an ignited spirit lamp. Mingling with the flame and round its rim were seen wreaths of darkness resembling an intensely black smoke. On lowering the flame below the beam the same dark masses stormed upwards. They were at times blacker than the blackest smoke from the funnel of a steamer; and their resemblance to smoke was so perfect as to lead the most practised observer to conclude that the apparently pure flame of the alcohol lamp required but a beam of sufficient intensity to reveal its clouds of liberated carbon.

But is the blackness smoke? This question presented itself in a moment. A red-hot poker was placed underneath the beam, and from it the black wreaths also ascended. A large hydrogen flame was next employed, and it produced those whirling masses of darkness far more copiously than either the spirit flame or poker. Smoke was therefore out of the question.

What then was the blackness? It was simply that of stellar space; that is to say, blackness resulting from the absence from the track of the beam of all matter competent to scatter its light. When the flame was placed below the beam the floating matter was destroyed *in situ;* and the air, freed from this matter, rose into the beam, jostled aside the illuminated particles, and substituted for their light the darkness due to its own perfect transparency. Nothing could more forcibly illustrate the invisibility of the agent which renders all things visible. The beam crossed, unseen, the black chasm formed by the transparent air, while at both sides of the gap the thick-strewn particles shone out like a luminous solid under the powerful illumination.

Oxygen, hydrogen, nitrogen, carbonic acid, so prepared as to exclude all floating particles, produce the darkness when poured or blown into the beam. Coal gas does the same. An ordinary glass shade placed in the air with its mouth downwards permits the track of the beam to be seen crossing it. Let coal gas or hydrogen enter the shade by a tube reaching to its top, the gas gradually fills the shade from the top downwards. As soon as it occupies the space crossed by the beam the luminous track is instantly abolished. Lifting the shade so as to bring the common boundary of the gas and air above the beam the track flashes forth. After the shade is full, if it be inverted the gas passes upwards like a black smoke among the illuminated particles.

If the nozzle of an ordinary pair of bellows be filled with cotton wool, not too tightly packed, the air urged through the wool is filtered of its floating matter, and it then forms a clean band of darkness in the illuminated dust.

A large and compact mass of cotton wool tied around the entry of the experimental tube was found competent to hold back the floating matter. A glass tube of small bore, plugged with cotton wool in the same manner as the nozzle of the bellows, proved to be a perfect filter of the dust-laden air. Being convenient in application and form, it was adopted and used as the dust filter throughout the investigations on the chemical reactions produced by light.

The above experiments, though at first looked upon by practical men as interesting only from a scientific point of view, have since borne much fruit, and have cleared the way for a complete conception of the relations of the floating matter in the air to the various phenomena of putrefaction and infection. Dr. Tyndall had this end fully in his mind, for in a discourse on the subject he proceeds:—

"But what, you may ask, is the practical good of these curiosities? And if you so ask, my object is in some senses gained, for I intended to provoke this question. I confess that if we exclude the interest attached to the observation of new facts, and the enhancement of that interest through the knowledge that by-and-by the facts will become the exponents of laws, these curiosities are in themselves worth nothing. They will not enable us to add to our stock of food, or drink, or clothes, or jewellery. But though thus shorn of all usefulness in themselves, they may, by leading the mind into places which it would not otherwise have entered, become the antecedents of practical consequences. In looking, for example, at this illuminated dust, we may ask ourselves what it is. How does it act, not upon a beam of light, but upon our own lungs and stomachs? The question at once assumes a practical character. We find on examination that this dust is organic matter—in part living, in part dead. There are among it particles of ground straw, torn rags, smoke, the pollen of flowers, the spores of fungi, and the germs of other things.

"The air of our London rooms is loaded with this organic dust, nor is the country air free from its pollution. However ordinary daylight may permit it to disguise itself, a sufficiently powerful beam causes the air in which the dust is suspended to appear as a semi-solid rather than as a gas. Nobody could, in the first instance, without repugnance place the mouth at the illuminated focus of the electric beam and inhale the dirt revealed there. Nor is the disgust abolished by the reflection that, although we do not see the nastiness, we are churning it in our lungs every hour and minute of our lives. There is no respite to this contact with dirt; and the wonder is, not that we should from time to time suffer from its presence, but that so small a portion of it would appear to be deadly to man."

And what is this portion? It was some time ago

the current belief that epidemic diseases generally were propagated by a kind of malaria, which consisted of organic matter in a state of *motor-decay;* that when such matter was taken into the body through the lungs or skin, it had the power of spreading there the destroying process which had attacked itself. Such a spreading power was visibly exerted in the case of yeast. A little leaven was seen to leaven the whole lump, a mere speck of matter in this supposed state of decomposition being apparently competent to propagate indefinitely its own decay. Why should not a bit of rotten malaria work in a similar manner within the human frame? In 1836 a very wonderful reply was given to this question. In that year Cagniard de la Tour discovered the *yeast plant*, a living organism, which when placed in a proper medium feeds, grows, and reproduces itself, and in this way carries on the process which we name fermentation. Fermentation was thus proved to be a product of life instead of a process of decay.

Schwann, of Berlin, discovered the yeast plant independently; and in February, 1837, he also announced the important result, that when a decoction of meat is effectually screened from ordinary air, and supplied solely with calcined air, putrefaction never sets in. Putrefaction, therefore, he affirmed to be caused by something derived from the air, which something could be destroyed by a sufficiently high temperature. The experiments of Schwann were repeated and confirmed by Helmholtz, Ure, and Pasteur. But as regards fermentation, the minds of chemists, influenced probably by the great authority of Gay-Lussac, who ascribed putrefaction to the action of oxygen, fell back upon the old notion of matter in a state of decay. It was not the living yeast plant, but the dead or dying parts of it, which, assailed by oxygen, produced the fermentation. This notion was finally exploded by Pasteur. He proved that the so-called "ferments" are not such; that the true ferments are organized beings which find in the reputed ferments their necessary food.

In a recent communication to the Royal Society, on the optical condition of the atmosphere in its bearings on putrefaction and infection, Professor Tyndall has shown that organic infusions of all kinds, when properly prepared, may be exposed to ordinary air for any length of time, and yet be preserved pure and free from putrefaction, the only condition necessary being the removal of the floating matter.

For this purpose a number of cases or chambers were constructed, each with a glass front, its top, bottom, back, and sides being of wood. At the back a little door is constructed to open and close on hinges, while into the sides are inserted two panes of glass facing each other. The top of the case is perforated by two apertures, into which is inserted air-tight two narrow glass tubes, intended to connect the interior space with the atmosphere. The tubes are bent several times up and down so as to intercept and retain the particles carried by such feeble currents as changes of temperature might cause to set in between the outer and inner air.

Into one or more rows of holes, pierced in the bottom of the case, is fixed air-tight large test tubes, intended to contain the liquid to be exposed to the action of the moteless air. The tubes thus inserted in a single case varied from three to twelve in number.

The interior of the case was coated with glycerine, and every part closed air-tight excepting the ends of the bent glass tubes. A powerful concentrated beam of light passed into the case through the side window showed the air within to be laden with floating matter. The case was then allowed to remain perfectly quiet for three days, when it was again examined by the concentrated beam, and was found to be optically empty. Thus three days of quietude had sufficed to cause all the floating matter to be deposited on the top, sides, and bottom of the case, where it was held fast by the coating of glycerine.

A strong and clear organic infusion was then introduced (through a pipette inserted air-tight through the top of the case) into the test tubes, and boiled for five minutes in a bath of oil. They were then abandoned to the action of the moteless air, maintained at a temperature of from 60° to 80° Fahr.; at the same time the same infusion, placed in similar test tubes, and boiled for five minutes in the oil bath, were exposed to the ordinary mote-laden air of the laboratory, kept at the same temperature as that in the closed case. After two or three days all the infusions exposed to the ordinary mote-laden air had fallen into a state of putrefaction, were very turbid, and swarming with life; while the infusion exposed in the closed case to the action of the moteless air, remained as pure and clear as the day it was introduced. In this pure and clear condition the infusion remained for a period of nearly five months, when the door at the back of the case was opened, and the mote-laden air being thus admitted, sufficed in three days to render the infusion turbid with putrefaction and rottenness.

In this manner infusions of a number of animal and vegetable substances, consisting of hay, turnips, tea, coffee, hops, malt, beef, mutton, pork, hare, rabbit, kidney, liver, fowl, pheasant, grouse, haddock, sole, mullet, salmon, cod, turbot, herring, whiting, eel, oysters, urine, &c., have been subjected to the action of air cleansed of its floating matter by self-subsidence, for a lengthened period of time. In every case the infusions have remained perfectly clear and unaffected, while the same infusion exposed to air containing the floating matter, were invariably smitten with putrefaction in two or three days.

In a similar manner various infusions have been exposed to the action of air freed of its floating matter by filtration through cotton wool, to air cleansed by its passage through the red-hot platinum tube, and to a vacuum; and in every case they have remained perfectly clear and unaffected.

The sole condition necessary to cause these long dormant infusions to swarm with active life, is the access of the floating matter of the air. After having remained for months as pellucid as distilled water,

the opening of the back door of the protecting cases, and the consequent admission of the floating matter, in three days rendered the infusions putrid and full of life.

Infusions of various kinds contained in 139 glass flasks, with necks drawn out and narrowed, were boiled for five minutes and hermetically sealed while boiling. The infusions thus prepared retain to this hour the clearness and colour which they showed on the day they were boiled, while specimens exposed to the laboratory air have long ago fallen into utter rottenness.

Experiments were conducted with regard to the distribution of the germs in the atmosphere. A tray of 100 tubes, containing hay, turnip, and beef, were exposed to the ordinary air, and from the irregular manner in which the tubes were infected, it may be inferred, that as regards quantity the distribution of the germs in the air is not uniform, but that they float through the air in groups or clouds, with space more sparsely filled between them.

Side by side with these researches and discoveries, and fortified by them and others, has run the *germ theory* of epidemic disease. The notion was expressed by Kircher, and favoured by Linnæus, that epidemic diseases are due to germs which float in the atmosphere, enter the body, and produce disturbance by the development within the body of parasitic life. The strength of this theory consists in the perfect parallelism of the phenomena of contagious disease with those of life. As a planted acorn gives birth to an oak competent to produce a whole crop of acorns, each gifted with the power of reproducing its parent tree; and as thus from a single seedling a whole forest may spring: so, it is urged, these epidemic diseases literally plant their seeds, grow, and shake abroad new germs, which, meeting in the human body their proper food and temperature, finally take possession of whole populations. Thus Asiatic cholera, beginning in a small way in the Delta of the Ganges, contrived in seventeen years to spread itself over nearly the whole habitable world. The development from an infinitesimal speck of the virus of small-pox of a crop of pustules, each charged with the original poison, is another illustration. The reappearance of the scourge, as in the cases of the *Dreadnought* at Greenwich, reported on so ably by Dr. Budd and Mr. Busk, received a satisfactory explanation from the theory which ascribes it to the lingering of germs about the infected place.

But by far the most interesting and important illustration of this filtering process is furnished by the human breath. If the ordinary air from the lungs be driven through a glass tube across the electric beam, the condensation of the aqueous vapour of the breath is shown by the formation of a luminous white cloud of delicate texture. It is necessary to abolish this cloud, and this may be done by drying the breath previous to its entering into the beam; or, still more simply, by warming the glass tube. When this is done the luminous track of the beam is for a time uninterrupted. The breath impresses upon the floating matter a transverse motion, the dust from the lungs making good the particles displaced. But after some time an obscure disc appears upon the beam, the darkness of which increases, until finally, towards the end of the expiration, the beam is, as it were, pierced by an intensely black hole, in which no particles whatever can be discerned. The air, in fact, has so lodged its dirt within the passage to the lungs as to render the last portions of the expired breath absolutely free from suspended matter. This experiment may be repeated any number of times with the same result. It renders the distribution of the dirt within the air-passages as manifest as if the chest were transparent.

If the lungs be emptied as perfectly as possible, and then filled with air inhaled through a handful of cotton wool, placed over the mouth and nostrils, on exdiring this air through the glass tube its freedom from floating matter is at once manifest. From the very beginning of the act of expiration the beam is pierced by a black aperture. The first puff from the lungs abolishes the illuminated dust and puts a patch of darkness in its place, and the darkness continues throughout the entire course of the expiration. When the tube is placed below the beam and moved to and fro the same smoke-like appearance as that obtained from a flame is observed. In short, the cotton wool, when used in sufficient quantity, completely intercepts the floating matter on its way to the lungs.

The application of these experiments is obvious. If a physician wishes to hold back from the lungs of his patient, or from his own, the germs by which contagious disease is said to be propagated, he will employ a cotton wool respirator. In the crowded dwellings of the London poor, where the isolation of the sick is difficult, if not impossible, the noxious air around the patient may, by this simple means, be restored to practical purity. Thus filtered, attendants may breathe the air unharmed. In all probability the protection of the lungs will be the protection of the entire system. For it is exceedingly probable that the germs which lodge in the air-passages, and which at their leisure can work their way across the mucous membrane, are those which sow in the body epidemic disease. If this be so, then disease can certainly be warded off by filters of cotton wool. And time will decide whether, in lung diseases also, the woollen respirator cannot abate irritation, if not arrest decay. M. Pasteur, in his most admirable work on this very important subject, has shown that the germs diminish as we ascend a mountain. By means of a cotton wool respirator, so far as the germs are concerned, the air of the Alps may be brought into the chamber of the invalid.

*Filtration of Air for Respiration.*—There are too many trades in England where life is shortened and rendered miserable by the introduction of matters into the lungs which might be kept out of them. Dr. Greenhorn has shown the stony grit deposited in the lungs of stone cutters. The black lungs of colliers is another case in point. In fact, a hundred obvious cases might be cited, and

others that are not obvious might be added to them. A manufactory in one of our large towns, where iron vessels are enamelled by coating them with a mineral powder, and subjecting them to a heat sufficient to fuse the powder, was visited some time ago. The organization of the establishment was excellent, but one thing only was needed to make it faultless. In a large room a number of women were engaged covering the vessels. The air was laden with the fine dust, and their faces appeared as white and bloodless as the powder with which they worked. By the use of cotton wool respirators these women might be caused to breathe air more free from suspended matters than that of the open street. A Lancashire seedsman stated some time ago that during the seed season of each year his men suffered horribly from irritation and fever, so that many of them left his service. He was advised to try the efficacy of cotton wool, and he found that by simply folding a little cotton wool in muslin and tieing it in front of the mouth, that he could pass through the season in comfort, and without a single complaint from one of his men.

In a colour factory where much emerald green was packed for export, the men were subject to fits of vomiting, and showed other symptoms of arsenical poisoning; by the use of cotton wool respirators all these annoyances disappeared.

The substance has also been turned to other uses. An invalid placed at night a little of the wool before his mouth, slightly moistening it to make it adhere; he thereby prolonged his sleep, abated the irritation of his throat, and greatly mitigated a hacking cough from which he had long suffered. In fact, there is no doubt that this substance is capable of manifold useful applications. An objection was urged against the use of it, that it became wet and heated by the breath. Mr. Carrick, of Glasgow, invented a respirator which, though since superseded, met this objection. It was a metal contrivance, the lower part of which could be filled with medicated substances. In this case it was filled with the cotton wool. It was provided with two valves; and when fitted tightly round the lips the air entered the mouth through the cotton wool by one of the valves, which was lifted during the act of inhalation. During exhalation this valve was closed, and the breath escaped through the other valve into the open air. The wool is thus kept dry and cool, the air in passing through it being filtered of everything it holds in suspension.

In the discourse before referred to Dr. Tyndall continues:—"We have thus been led by our first unpractical experiments into a thicket of practical considerations. In taking the next step a personal peculiarity had some influence upon me. The only kind of fighting in which I take delight is the conflict of man with nature. I like to see a man conquer a peak or quench a conflagration. I remember clearly the interest I took twenty years ago in seeing the firemen of Berlin contending for mastery with a fire which had burst out somewhere near the Brandenburger Thor; and I have often experienced the same interest in the streets of London. Admiring as I do the energy and bravery of our firemen, and having heard that smoke was a greater enemy to them than flame itself, the desire arose of devising a fireman's respirator. Firemen have hitherto been dependent on the smoke jacket, of which Captain Shaw says:—'It is very useful for extinguishing fires in vaults, stopping conflagrations in the holds of ships, and penetrating wells, quarries, mines, cesspools, &c.; any places, in short, where the air has become unfit for respiration. but its drawback is that it requires the use of an engine or air-pump, and consequently is of no service to one man alone. For this latter reason smoke-jackets, although very effective for enabling us to get into convenient places for extinguishing fires, have very rarely proved of any avail for *saving life*.'

"Now it is that very want that I thought ought to be supplied by a suitable respirator. Our fire-escapes are each in charge of a single man, and I wished to be able to place it in the power of each of those men to penetrate through the densest smoke into the recesses of a house, and there to rescue those who would otherwise be suffocated or burnt. I thought that cotton wool, which so effectually arrested dust, might also be influential in arresting smoke. It was tried; but though found soothing in certain gentle kinds of smoke, it was no match for the pungent fumes of a resinous fire, which, according to Captain Shaw, evolves the most abominable smoke with which he is acquainted. I cast about for an improvement; and in conversing with my friend Dr. Debus, he suggested the use of glycerine to moisten the wool and render it more adhesive. In fact, this very substance had been employed by the most distinguished advocate of the doctrine of spontaneous generation. M. Pouchet, for the purpose of catching the atmospheric germs. He spread a film of glycerine on a plate of glass, urged air against the film, and examined the dust which stuck to it. The moistening of the cotton wool with this substance was a decided improvement; still the respirator only enabled us to remain in dense smoke for three or four minutes, after which the irritation became unendurable. Reflection suggested that in combustion so imperfect as the production of dense smoke implies, there must be numerous hydrocarbons produced, which, being in a state of nature, would be very imperfectly arrested by the cotton wool. These, in all probability, were the cause of the residual irritation; and if these could be removed a practically perfect respirator might possibly be obtained.

"All bodies possess the power of condensing in a greater or less degree gases and vapours upon their surfaces, and when the condensing body is very porous, or in a fine state of division, the force of condensation may produce very remarkable effects. Thus, a clean piece of platinum foil placed in a mixture of oxygen and hydrogen so squeezes the gases together as to cause them to combine; and if the experiment be made with care the heat of com-

bination may raise the platinum to bright redness, so as to cause the remainder of the mixture to explode. The promptness of this action is greatly augmented by reducing the platinum to a state of fine division. A pellet of "spongy platinum," for instance, plunged into a mixture of oxygen and hydrogen causes the gases to explode instantly. In virtue of its extreme porosity, a similar power is possessed by charcoal. It is not strong enough to cause the oxygen and hydrogen to combine like the spongy platinum, but it so squeezes the more condensable vapours, and also acts with such condensing power upon the oxygen of the air, as to bring both within the combining distance, thus enabling the oxygen to attack and destroy the vapours in the pores of the charcoal. In this way effluvia of all kinds may be virtually burnt up; and this is the principle of the excellent charcoal respirators invented by Dr. Stenhouse. Armed with one of these, you may go into the foulest-smelling places without having your nose offended.

"But while powerful to arrest vapours, the charcoal respirator is ineffectual as regards smoke. The particles get freely through the respirator. In a series of them tested, from half a minute to a minute was the limit of endurance. This might be exceeded by Faraday's method of emptying the lungs completely, and then filling them before going into a smoky atmosphere. In fact, each solid smoke particle is itself a bit of charcoal, and carries on it and in it its little load of irritating vapour. It is this, far more than the particles of carbon themselves, that produces the irritation. Hence two causes of offence are to be removed: the carbon particles which convey the irritant by adhesion and condensation, and the free vapour which accompanies the particles. The moistened cotton wool I knew would arrest the first, fragments of charcoal I hoped would stop the second. In the first fireman's respirator Mr. Carrick's arrangement of two valves, the one for inhalation, the other for exhalation, were preserved; but the portion of it which holds the filtering and absorbent substances was prolonged to a depth of four or five inches. On the partition of wire gauze at the bottom of the space which fronts the mouth is placed a layer of cotton wool moistened with glycerine, then a thin layer of dry wool, then a layer of charcoal fragments, a second thin layer of dry cotton wool, succeeded by a layer of fragments of caustic lime. In the densest smoke the layer of lime was not found necessary in a flaming building; indeed, the mixture of air with the smoke never permits the carbonic acid to become so dense as to be irrespirable; but in a place where the gas is present in undue quantity, the fragments of lime would materially mitigate its action.

"In a small cellar-like chamber, with stone flooring and stone walls, the first experiments were made. We placed there furnaces containing resinous pinewood, lighted the wood, and placing over it a lid which prevented too brisk a circulation of the air, generated dense volumes of smoke. With our eyes protected by suitable glasses, my assistant and I remained in this room for half an hour and more, when the smoke was so dense and pungent that a single inhalation through the undefended mouth would be perfectly unendurable: and we might have prolonged our stay for hours. Captain Shaw and three men of the fire brigade made trial of the respirator under the same conditions. On coming out they said that they had not suffered the slightest inconvenience; that they could have remained all day in the smoke."

The following are some of the practical adaptations of Professor Tyndall's dust and smoke filtering materials:—

*The Smoke Cap of Captain Shaw.*—This smoke cap consists mainly of two parts, called respectively the hood and the respirator. The hood is made of the best dressed calf skin blacked, cut in sections, and closed with air-tight joints, each part overlapping the next to the extent of half an inch, and the sections strongly sewn together with two separate rows of saddlers' stitching. The skull part is fitted to the shape of a man's head, and is about 24 inches in circumference at the widest part; underneath this there is a band about 2 inches deep, forming a kind of yoke or apron piece about 6 inches deep, shaped to fit on a man's chest and shoulders under a tunic.

To facilitate the putting on and taking off of the hood, there is an opening down the whole of the back part, from the crown to the neck, and on each side of this opening is a row of four eyelet holes with brass bushes. Through these holes there is rove as a lacing leather thongs, the ends of which go round to the front, and after passing through a small metal lining are knotted at the ends below two wooden knobs, to prevent their being pulled back through the ring. When the hood has been put on the thongs are pulled in front, and rendering through the eyelet holes, draw the whole of the skull part close to the head. The opening at the back is fitted with a piece of what is commonly known as waterproof sheeting, a thin air-tight material which occupies very little space, and although wide enough to allow the head to enter freely is easily folded away by the drawing of the thongs. The lower flap or apron part is tucked in under the collar of a tunic, so as to form an air-tight joint sufficient for the purpose.

To the front of the hood inside is attached, by means of brass rivets, a tinned sheet of metal shaped to fit the front of a man's face, from the bridge of the nose to the chin. Into this, opposite to the mouth, is fixed a hard wooden mouthpiece.

At a distance of about 4 inches above the mouthpiece there are fixed a pair of curved eye-glasses of the best clear glass, set with cement in brass fittings, which are attached by screws to curved metal frames riveted on the inside of the hood.

The respirator consists of two parts, the valve chamber and the filter tube.

The valve chamber is a brass tube 2 inches long and 2 inches in diameter, with an upper and lower valve plate. Between the two plates is soldered and

riveted a brass connecting piece, by means of which the respirator is attached to the hood.

Each of the valve plates is fitted with three ebonite ball valves, half an inch in diameter, turned perfectly round, and without the slightest projection or rim in any part. The openings in the plates are $\frac{5}{16}$th inch in diameter, and are cut, that the seatings embrace at least one-third of the valves. The seatings, which are separate pieces, are screwed into the plates, and are most carefully bevelled out, so that the valves shall make an exact fit.

Above the valves there is screwed on a cap-plate, which protects the valves from injury. It is pierced round the edge with twenty-eight holes for the escape of the discharged air.

The filter tube, which is screwed to the valve-chamber, is also of brass. It is of the same diameter as the valve-chamber, and is 4 inches long. Across its upper end is soldered a piece of fine wire gauze, which prevents the filtering materials passing. Over its lower end there is screwed on a brass ring or cup, with a similar piece of wire gauze; this, while allowing the air to pass, prevents the filtering materials from falling out.

The charge for the filter consists of the following:—Half an inch deep of dry cotton wool, an inch deep of the same wool saturated with glycerine, half an inch deep of dry wool, an inch deep of fragments of charcoal, and an inch deep of dry wool. In filling, the respirator is turned upside down, and the materials are packed so as to fill every part of the chamber, and pressed down as tightly as experience shows to be compatible with facility of breathing when in use. After this the grating cap is screwed on, and the filter is then ready for use. A layer of caustic lime is introduced when using the apparatus in carbonic-acid charged atmospheres.

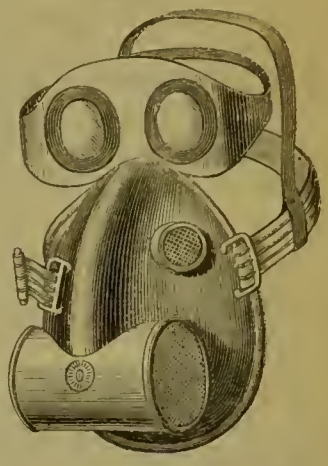
The total weight of this respirator when charged and ready for use is $2\frac{1}{2}$ lbs.

In putting on the smoke cap it is held with the face part downward, the hood is then slipped over the head, and as soon as the top rests on the top of the head, the wooden mouthpiece is adjusted in the mouth; this brings the eye-glasses and other parts into their proper positions. The lower flaps are then tucked under the tunic of the wearer, and the thongs hanging in front are tightly pulled until the lacing at the back draws the skull part closely round the head. After this the tunic is buttoned up to the neck, the helmet is put on, and then all is in readiness for working in a densely smoke-laden atmosphere.

*Face Piece and Respirator.*—This apparatus, which is represented in the annexed cut, is a thin soft metal cover, having fixed around its edge a soft india-rubber tube filled with water. When placed upon the face of the wearer, it fits air-tight around the nose and mouth. In the upper part of one side is fixed a cylinder of ebonite, of about an inch in diameter, having a $\frac{3}{8}$th of an inch hole bored through it. Attached to, and covering the outer end of this cylinder (which is perfectly flat and smooth), is a flap of vulcanized india-rubber. This flap lies in close contact to the smooth end of the cylinder, and forms an excellent respiratory valve. This valve is protected from injury by a wire gauze cover.

To the lower part of the face piece is attached the filter tube, a tin cylinder $3\frac{1}{2}$ inches long and 2 inches in diameter, one end of which opens into the interior of the face piece. The other end is fitted with a movable wire gauze cap, which prevents the filtering materials falling out. Associated with the face piece, but not attached to it, is a broad vulcanized india-rubber band, into which is inserted two ebonite rings. Into the ebonite rings are fitted air-tight strong curved glasses, similar to watch glasses. The arrangement of the materials in the filter chamber are the same as used in the filter chamber of the smoke cap.

Fig. 1.



In adjusting the apparatus, the vulcanized india-rubber band is stretched over the upper part of the face by means of an elastic band which passes round the head. The curved glasses are adjusted to suit the position of the eyes, and the broad band of india-rubber being thus pressed into the indentations of the face, completely protects the eyes from smoke.

The metal face piece is now placed over the nose and mouth and secured in position by means of an elastic strap, which passes from one side of the face piece around the head, and is made fast to a buckle attached to the other side. A band attached to the elastic strap fits over the top of the head and prevents the face piece falling below its proper position.

During inspiration the air passes through the filtering materials in the tin cylinder into the face piece, to the mouth and nose. During expiration, the air from the lungs is ejected through the expiratory valve into the open air.

The advantage of this form of smoke respirator is, that the wearer can respire through the nose as well as through the mouth. Also, the mouth being perfectly free there is no excessive secretion of saliva, which in the smoke cap (owing to the wearer respiring only through a wooden tube held in the mouth) is considerable.

*Dust Filter.*—The face piece above described is fitted with a tin cylinder of the same form, but of smaller dimensions than that used for the filtration of smoke. It is entirely filled with dry cotton wool. When in use, it is attached to the face of the wearer in the same manner as described above. The glass protectors for the eyes are, of course, not used.

*Cottrell's Face Piece.*—The most recent form of the smoke respirator is constructed (with exception of

the filter chamber and the glass eye-protectors) entirely of vulcanized india-rubber.

A sheet of vulcanized india-rubber about 10 inches long and 7 inches wide has (at about 2 inches from one edge, and midway from each end) an aperture cut, of such shape and dimensions as to allow the lips to protrude. Above this another aperture is cut, which allows the nose to pass easily through it. On each side of the nose aperture, and a little above it, a circular hole is cut corresponding to the position of the eyes.

A bent tin cylinder 4½ inches long and 2 inches diameter (having a curvature nearly corresponding to the curvature of the face) is firmly and securely fixed opposite to, and forming a closed chamber around the mouth aperture, by means of strips of sheet india-rubber.

The nose aperture is covered with sheet rubber, forming a chamber sufficiently large for the protruding nose. The lower ends of the nose cover are attached to the rubber sheet supports of the tin cylinder, in such a manner as to connect the nose and mouth apertures by a small chamber.

Into each hole corresponding to the eyes a circular curved glass about 1¾ inch diameter (similar to a watch glass), held in a suitable fitting, is inserted.

One end of the tin cylinder is closed by an india-rubber valve, opening outwards. This valve is protected by a movable wire gauze covering.

The side of the tin cylinder, a little below the valve, is pierced by a hole, covered with wire gauze, which opens into the mouth chamber. The other end of the tin cylinder is fitted with a movable wire gauze covering, which prevents the filtering materials from falling out.

The filtering materials are the same as previously employed.

The apparatus when in use is secured to the head of the wearer by two narrow elastic straps, one of which passes from the upper part of the apparatus round the head; the other passes from the lower part of the apparatus round the neck. With a little pressure of the straps, the flexible sheet india-rubber of the face piece is drawn air-tight into the indentations of the face, and around the mouth and nose.

During inspiration the valve is closed by atmospheric pressure, and the air passes through the filtering materials in the tin cylinder through the hole (below the valve) opening into the mouth chamber, to the mouth and nose. During expiration the air is ejected from the lungs through the outward opening valve into the open air.

The total weight of the apparatus when charged with the filtering materials is about 9 ozs.

Its advantages over previous forms are its lightness, simplicity of construction, and cheapness; the ease and rapidity of adjustment; no undue heating of the head, the face only being covered; no chance of derangement by the bursting of water tubes, &c., as none are used. As in the face-piece, the wearer can respire through the nose as well as through the mouth. In this case also, the mouth being free from any air-tube, there is no excessive secretion of saliva.

*Cottrell's Dust Filter.*—This is an apparatus constructed of very light vulcanized rubber. It is similar in shape and construction to the smoke respirator, but the part above the nose, containing the curved glass protectors, is removed. Wire springs are introduced on each side of the nose, so as to press the edges of the rubber sheet into the indentations of the face. The cotton wool chamber is much smaller than the filter chamber of the smoke respirator, and is constructed of light wire gauze, covered with thin sheet rubber. In use, it is held in position by a single elastic band passing round the head. The whole thing, when charged complete, is exceedingly light, and can be worn for a long period without inconvenience.

*Natural Disinfectants.*—Pure air is a disinfectant, and shows its beneficial action by the effects of good ventilation, which carries away, starves, and destroys the organic germs which cause infection. Stagnant air is incapable of disinfecting the usual vitiation of towns, or even of the country, with sufficient rapidity, much less can it purify a room subjected to any source of foulness; but when a current comes and mixes the vapours from the earth with the enormous expanse of air above, or carries them away to the ocean, there is then given to them space for purification, the particles are disintegrated thoroughly and oxidized, and living germs die for want of nutriment, so that before the same air can again come into contact with human beings, it is rendered perfectly innocuous.

Under this head comes ventilation, details of which as a purely mechanical means of disinfection would be out of place here. Nevertheless it is a study of great importance, and in the construction of large rooms, hospital wards, and even in ordinary dwellings, it should have special attention, as health is dependent on its being thorough.

Water is the next great natural disinfectant. It is true that moist bodies decay more rapidly than others, and that a certain amount of humidity is essential to cremacausis; water is, therefore, both a great corrupter and a great purifier, according to the circumstances of the case. Water in quantity is a disinfecting agent by the simple act of washing; this is its mechanical, and probably its most important effect. In this way each shower of rain becomes a natural disinfectant to the atmosphere, bringing down with it the floating organic substances and diffused gases. Every river is a great remover of substances capable of decomposition, but, however pure it may be, if water be allowed to remain stagnant for a short time, it will be found that there will soon be matter enough in it to cause putrefaction. The ocean also disperses the decaying material abroad, removes it from the land, mixes it with purer water, dashes it about in the air, and thus produces purification. Water is the only fluid that will communicate to the skin the feeling of freshness, an accompaniment of cleanliness, and so exceedingly liked by every person that it must be pronounced a most natural and wholesome condition; indeed, so much is freshness generally esteemed, that it stands

in the language as a very type of vigour and beauty. In all cases where water will remove the evil, it ought to be used as the most efficient and agreeable.

Soil is another great disinfectant, and, in conjunction with air and water, is the most efficient of all. The water carries into the soil the impurities it meets with; the air penetrates the water, and is powerfully retained by the soil, and by this means the organic and putrid substances are brought into contact with the oxygen, and oxidation is made forcibly to take place. Hence a field manured with the most fetid compounds gives off no smell after the lapse of a few days, or even hours, and the water drained from it possesses no special odour, provided the drains be sufficiently deep. Were it not for this agency men and animals would soon render the country uninhabitable. From this cause, too, the soil of a city is freed from impurities, and instead of albuminous bodies containing nitrogen being found in it, the nitrogen is oxidized, and nitrates are formed, except in instances where the abundance of animal matter is more than can be acted on by the soil.

The greatest remedial measures that can be adopted for the general disinfection of a country are, therefore, air, water, and land drainage, all to some extent under the power of man; the latter almost entirely so.

There are two agencies, partly natural and partly artificial, which check decomposition, and in suitable conditions entirely arrest it; these are heat and cold: it is necessary to treat them as distinct, because they present themselves as such. The former prevents decay by drying, as well as by changing the chemical state of substances.

It has been assumed that a temperature of 200° Fahr. was sufficient to destroy the living organisms in fetid matter; but the experiments of the late Dr. Crace Calvert, F.R.S., tend rather to prove that heat alone, even far above that temperature, does not entirely render it innocuous, but merely checks the development of protoplasmic life; and his experiments are confirmed by Dr. Beale, who states that "living forms might live though exposed under certain conditions to a temperature of 350° Fahr."

It is still a matter of keen controversy as to the temperature required to destroy the vitality of living germs and minute infusorial matter so as to render infectious matter inert.

Heat should be employed for disinfecting purposes when available, and if used in conjunction with certain artificial disinfectants, and according to the plan adopted in several large towns, in the disinfecting stoves and ovens for infected clothing, all chance of infection will be removed.

Cold, of all antiseptics and disinfectants, is the most powerful, since growth and decomposition, the result of germ growth, cannot go on when the temperature sinks below about 35° Fahr.; it can, however, seldom be had recourse to, because not completely under control; and when it can be commanded, it cannot be applied to living beings, and it may be added, that when it is removed the former condition again sets in. The ice-buried animals in the North are a well-known example. Under the influence of intense cold chemical action ceases; particles of flesh remain firmly united, as if they were in reality what they resemble in hardness—a piece of rock.

*Artificial Disinfectants.*—So many different substances have at various times been proposed and used with more or less effect as disinfectants, that it would be impossible in the limits of our space to give a description of each, and therefore we shall confine ourselves to the following as being the more important ones:—

| | |
|---|---|
| Carbolic acid. | Chlorides of zinc and lime. |
| Cresyl alcohol. | Sulphurous acid and sulphites. |
| Salicylic acid. | Metallic sulphates. |
| Chlorine. | Permanganate of potash. |

*Carbolic acid*, *Phenol*, *Phenyl hydrate*, *Phenyl alcohol*, *Phenic acid*, *Coal-tar creosote* ($C_6H_6O = C_6H_5OH$).—This body is contained in coal tar. It is prepared commercially by distilling the tar until anthracene makes its appearance. The resulting volatile oils are redistilled, and that part which is volatilized between 150° and 200° C. collected, mixed with potash liquor and powdered potassium hydrate, by which it is precipitated as a white crystalline powder. This is dissolved in hot water, when an oily matter rises to the surface, which is skimmed off. The alkaline liquor is then neutralized with hydrochloric acid, and the impure phenyl hydrate which rises to the surface is washed with water and rectified over chloride of calcium. Addition of a few crystals of pure phenol to that portion of the distillate which comes over between 186° and 188° causes a large part of the phenol to solidify at once, and thus materially shortens the operation. It can then be purified by sublimation.

Commercial carbolic acid is generally very impure.

The liquid acid is frequently adulterated with tar oils, which decrease its value considerably, and seriously deteriorate its disinfecting powers, rendering it at the same time insoluble or nearly so in water.

The following is a ready method of testing its purity.

Put one volume of the liquid to be tested into a graduated glass measure, and add two volumes of a solution of caustic soda 14° Twaddell, at 60° Fahr., and shake them well together for about a minute. If the carbolic acid is genuine it will be dissolved in the caustic soda solution, and the solution will appear bright and clear; but if any tar oils are present they will either float on the surface or sink to the bottom of the tube, according as they are light or heavy oils of tar. Carbolic acid containing tar oil should be rejected.

As a convenient form for disinfecting purposes, disinfecting powder consisting of lime and carbolic acid is prepared, and according to the percentage of carbolic acid it contains does its efficacy depend.

The following is an easy method of determining the percentage contained by the powder, as the various carbolic disinfecting powders offered for sale contain from 1 to 15 per cent. of carbolic acid.

Weigh 1000 grs. of the powder, and place it in a small tubulated retort.

Heat the retort gradually until the liquid distilled ceases to drop (a brisk heat is required towards the end of the operation).

Collect the distillate, which will condense in the tube of the retort, in a graduated cylinder grain measure, and allow it to settle for an hour, when the amount of oily liquid and water may be read off.

The oily liquid should represent the amount of carbolic acid, and to determine if it consists of carbolic acid, to one volume of it add two volumes of a solution of pure caustic soda, 14° Twaddell's hydrometer, at 60° Fahr., which will entirely dissolve the carbolic acid.

If any remains undissolved it will probably consist of either heavy or light oil of tar, the most frequent adulterants of carbolic acid, and in some cases entirely substituting it.

The above process will, if carefully worked, give within one per cent. of the amount of carbolic acid really contained by the powder.

*Cresol, Cresylic phenol, Cresyl alcohol* ($C_7H_8O = C_6H_4OH,CH_3$) is likewise contained in coal tar; it is prepared by fractional distillation of coal-tar creosote, as a liquid boiling at 203° C. It is a homologue of phenyl alcohol, into which it is decomposed by repeated distillation by the oxidizing action of the air in an atmosphere of hydrogen: distillation for any number of times leaves it unaltered.

*Salicylic acid* ($C_7H_6O_3 = C_6H_4\begin{Bmatrix}OH\\COOH\end{Bmatrix}$), *meta-oxybenzoic acid.*—Salicin ($C_{13}H_{18}O_7$) is a glucoside or neutral vegetable principle, which was discovered by Leroux in 1830 in the bark of the willow, *salix*, whence its name. It was afterwards found in various species of poplar, and in other trees and plants. Piria prepared salicylic acid from salicin by melting it with potassium hydrate. Löwig and Weidmann found that it was contained in the flowers of *Spiræa ulmaria* (meadow sweet); and later Procter showed that oil of winter green, *Gaultheria procumbens*, was really a salicylous ether, and from this source salicylic acid was obtained by Cahours.

Within the last few years German chemists have investigated its properties, and have discovered its powerful action as an antiferment and antiseptic. These reactions producing a demand for it, Kolbe and Lautemann sought for an organic compound which, from its elementary composition, might be split up into the desired acid. This substance they found in phenol (carbolic acid). On dissolving sodium in hot phenol in the presence of a stream of carbonic acid, there is always formed, besides sodic salicylate, more or less sodic carbonate and phenylate. They also observed that the more of the former salt there was, the less was found of the two latter. Moreover, a product rich in sodic phenylate, and relatively poor in sodic salicylate, yields the latter salt freely when further heated in a stream of carbonic acid.

Upon these reactions Kolbe founded a process which is now carried out on a large scale; and which he describes as follows:—

Saturate exactly commercial crude soda lye of known strength with crystallized carbolic acid previously fused, and evaporate in a shallow iron vessel, taking care that the sticky dough-like mass does not adhere to the bottom of the vessel as it becomes dry; the mass is constantly crushed with pestles until the sodic phenylate remains as a perfectly dust-dry powder. It is always reddish yellow in colour, perhaps on account of partial decomposition by the oxygen of the air during the evaporation, is very hygroscopic, and must while yet hot be excluded the air.

If the sodic phenylate is moist, or contains either free alkali or carbolic acid, the result is not good, a dark-coloured substance being formed, which, when it undergoes the final process of treatment with carbonic acid gas, gives far less salicylic acid than is in accordance with the amount of calculated phenylate present.

The dry sodic phenylate is then either filled into the retorts at once, or it may be kept for further treatment by filling it when hot in vessels which can be hermetically sealed.

After filling the retorts the contents are slowly heated to 100° C., and when this temperature is reached, a slow current of perfectly dry carbonic acid gas is allowed to enter the retort. The temperature is then slowly increased to 180° C., and may, towards the end of the operation, reach from 220° C. to 250° C.

About an hour after beginning the operation carbolic acid will begin to distil, and the process may be considered finished if, at the latter mentioned temperature (220° to 250° C.), no more carbolic acid distils. It will then be found that the distilled carbolic acid amounts to just half of the original quantity employed.

The residue in the retort is basic sodic salicylate, which is dissolved, and which, on being acidified with an acid, yields a brownish coloured crystalline precipitate of salicylic acid.

The further process of decolorizing the salicylic acid was not described by Kolbe, but Rautert states that this colouring may be removed by heating it to 170° C. in a retort, and then injecting a current of superheated steam of the same temperature. Colourless salicylic acid distils at once, and after a short time nothing but a trace of a black resinous mass remains in the retort. The apparatus must be arranged in such a manner that the neck of the retort can by mechanical means, as for instance a movable wire, be kept free from crystals.

An exceedingly interesting reaction takes place, according to Endemann, if potash is substituted for soda in the above process; the resulting acid is under these circumstances not salicylic, but pure oxybenzoic acid, a substance which is isomeric with salicylic acid, and according to Kolbe's experiments without any disinfecting properties whatever. If the process, however, is carried out with potash, but at a temperature not exceeding 145° C., Hartmann states that the resulting acid is in this case also salicylic acid.

Baryta, strontia, lime, and magnesia, furnish at 220° C. salicylic acid, and therefore act like soda.—Ost.

If in Kolbe's process for the manufacture of salicylic acid, cresol (cresyl alcohol, $C_7H_8O$) be substituted for phenol, cresotic acid is formed, which shares with salicylic acid the disinfecting properties. A non-crystalline carbolic acid containing cresol may, therefore, be used for the manufacture of salicylic acid, as the disinfecting properties of the product are not diminished by its containing some cresotic acid.

For medical internal use, however, the two products ought to be kept strictly apart until the physiological effects of each have been well defined.

Salicylic acid is odourless. It has a sweetish and astringent after taste, though itself tasteless. It is sold in minute broken acicular crystals, which give it the appearance of a granular powder, soft and smooth under the pestle or knife, but somewhat rough when rubbed between the fingers. It is insoluble in cold, but very soluble in hot water; and the water of a hot solution retains when cold, in proportion to its temperature, from about 1 part in 250 to 1 part in 500 in solution. The presence of various neutral salts in small proportion in the water render it more soluble.

Up to this time sodic phosphate has been used in Germany to render it more soluble in water for medicinal purposes, and it is said that 3 parts of sodic phosphate will render 1 part of the acid easily soluble in 50 parts of water. It is much more soluble in alcohol and ether than in water. It melts at about 125° C. (257° Fahr.) and sublimes at 200° C. (392° Fahr.).

Salicylic acid is used for medical and surgical purposes either dry or in solution. When used dry it is mixed with some diluent, generally starch, and sprinkled on the wound or dressings in the form of a very fine powder.

When used in solution either for spraying surfaces or for washes or gargles, it is used in tepid solution of about 1 part in 300 parts of water.

Salicylic acid is effective as an antiseptic in very small quantities, and is at the same time entirely devoid of irritant action upon living tissues. It is not caustic in small quantity and never produces inflammation. It averts and prevents processes of decomposition both vital and chemical—vital, or those in which living organisms have a part, such as that produced by yeast, and many of those which occur in putrefaction; and chemical, or those which occur independently of vitality, as the production of the volatile oils in mustard and bitter almonds, the effect of diastase, &c. In quantities thoroughly effective for disinfecting purposes it is entirely odourless, tasteless, and is not poisonous.

Disinfection. — Phenol and cresol, which are closely allied, hold the foremost place among disinfectants, both on account of their cheapness and efficiency, and because they can be employed either in solution or vapour.

These two substances are derivatives of coal tar. The carbolic acid usually employed for disinfecting purposes is either in the form of detached crystals, containing a large percentage of carbolic acid with a small percentage of cresyl alcohol, soluble in about 60 parts of water; or in a liquid form, containing a smaller percentage of carbolic acid with a larger percentage of cresyl alcohol, and soluble in about 80 parts of water.

A very dilute solution of either of these acids is sufficient to destroy infusorial life. From experiments made at the Morgue in Paris, M. Devergie remarks, "that during the heat in summer, when putrefying corpses in the Morgue continually emit a quantity of noxious gases that cannot be removed by ventilation, or destroyed by chlorine or bleaching powder, we decided to prevent their production by trying to destroy the vitality of the germs of putrefaction, and thus prevent decomposition itself. We effected this by dissolving 1 litre of carbolic acid in a reservoir holding 1000 litres of water, and irrigating the bodies with the solution thus made; putrefaction was completely stopped, and disinfection was even obtained after reducing the quantity of acid by one half. M. Devergie points out that water containing $\frac{1}{1000}$th part of carbolic acid proved sufficient during the intense heat of a Paris summer to disinfect the dead-house without aid of any shaft, when six or seven bodies were lying there."

The late Dr. F. Crace Calvert, F.R.S., gives the following table of experiments made by him with several antiseptics. He placed solutions of albumen and flour paste in uncorked bottles, and added to them the antiseptics with the following results:—

| Antiseptic employed. | Percentage of Antiseptic. | Time in which it acquired an offensive odour. Temperature 70° to 80° Fahr. Albumen. | Flour paste. |
|---|---|---|---|
| Chloride of aluminium (made lately), | 2 | 9 days. | 10 days. |
| Chloride of zinc, | 2 | 15 " | Remained sound. |
| Chloride of lime, | 5 | 16 " | 14 days. |
| Permanganate of potash, | 5 | 4 " | 6 " |
| Tar oil, | 2 | 11 " | 25 " |
| Carbolic acid, | 2 | Remained sound. | Remained sound. |
| Cresyl alcohol, | 2 | Remained sound. | Remained sound. |
| None, | - | 5 days. | 7 days. |

He further adds, "The above table clearly shows that the only true antiseptics are carbolic acid and cresyl alcohol, and these results coincide with those obtained by Mr. William Crookes, F.R.S., Dr. Angus Smith, F.R.S., and Dr. Sansom. For these two acids continued their action till the albumen solution and paste dried up.

"It follows that if deodorizers are merely required for removing the noxious odour from any mass of matter in a state of decay or decomposition, they may be used with advantage; such are chlorides of manganese, lime, sulphate of iron, permanganate of potash, and aluminium. But if it is desirable to prevent the decomposition of organic matter (and in my opinion this is the point to be aimed at, for prevention is better than cure), then carbolic and cresylic acids are the only two substances which attained this object."

As the products given off from decaying organic matter are well known to facilitate the decomposition of similar classes of substances to themselves, if placed in close proximity (no doubt by the atmosphere conveying the germs), Dr. Crace Calvert made the following experiments with the view of ascertaining which of the undermentioned substances would possess the most active power in destroying such germs, and thus preserving the animal substance from decay. At the bottom of wide-mouthed pint bottles he placed a known quantity of each of the antiseptics, and suspended over them by a thread a piece of sound meat, and by daily examination it was easily ascertained when the meat became tainted or putrid. The following table gives the results obtained:—

| Antiseptic. | Became tainted. | Putrid. |
|---|---|---|
| Permanganate of potash, | 2 days | 4 days. |
| Chloride of aluminium, | 2 days | 10 days. |
| Chloride of lime, | 14 days | 21 days. |
| Tar oil, | 16 days | 25 days. |
| Chloride of zinc, | 19 days | — |
| Carbolic acid, | Did not become tainted, but dried up, and became quite hard. | |
| Cresyl alcohol, | Do., | do. |

The comparative value of antiseptics is also shown by the following carefully executed series of experiments made by S. Bucholtz, to determine the different amounts of each which would check the putrefaction of a liquid of known composition. The Pasteur's liquid he used was a solution of 10 grammes of common sugar, 1 gramme of tartrate of ammonia, and half a gramme of phosphate of potassium in 100 c.c. of distilled water. The amount of any antiseptic needed to prevent the putrefaction of this liquid was easily determined by filling a number of tubes with it, adding different amounts of the antiseptic to them, and then watching the results of their impregnation with a few drops of a decomposing infusion of tobacco.

The results of these experiments are given in the following tables:—

Smallest amount which prevented the development of bacteria:—

| | 1 part in |
|---|---|
| Corrosive sublimate, | 20,000 |
| Thymol, | 2,000 |
| Sodium benzoate, | 2,000 |
| Creosote, | 2,000 |
| Benzoic acid, | 1,000 |
| Methyl salicylic acid, | 1,000 |
| Salicylic acid, | 666 |
| Eucalyptol | 666 |
| Sodium salicylate, | 250 |
| Carbolic acid, | 200 |
| Quinine, | 200 |
| Sulphuric acid, | 151 |
| Boracic acid, | 133 |
| Cupric sulphate, | 133 |
| Hydrochloric acid, | 75 |
| Zinc sulphate, | 50 |
| Alcohol, | 50 |

Smallest amount which would stop putrefaction and render the bacteria incapable of further development when removed to fresh Pasteur's solution:—

| | 1 part in |
|---|---|
| Chlorine, | 25,000 |
| Iodine, | 5,000 |
| Bromine, | 3,333 |
| Sulphurous acid, | 666 |
| Salicylic acid, | 312 |
| Benzoic acid, | 250 |
| Methyl salicylic acid, | 200 |
| Sulphuric acid, | 161 |
| Creosote | 100 |
| Carbolic acid, | 25 |
| Alcohol, | 4.5 |

The late Dr. Letheby states that in his experiments in the city of London, he found that a very small quantity of carbolic acid in the sewers prevented decomposition, and that a solution of one per cent. of it upon meat arrested putrefaction.

Dr. Bakewell, formerly a medical officer of health for Trinidad, makes the following statements with regard to carbolic acid.

"I can bear testimony to the efficacy of carbolic acid in removing all offensive smell, and its usefulness as a topical stimulant for weak or sloughing sores. I employed it largely as a disinfectant, and particularly for cases of yellow fever, during the late epidemic in Trinidad. I had it used in all the houses where cases occurred; and when I had to inspect drains, cesspools, or places where there had been contagious sickness, I always carried a little about with me to smell whilst inspecting; without this I could not have performed my duties, so fearful are some of the stenches in the tropics. My assistants were glad to adopt the same plan.

"The advantages peculiar to carbolic acid over other disinfectants are: 1st, volatility; 2nd, cheapness; 3rd, its smell, which enables one always to know when a sufficiency has been used; 4th, the fact that it can be employed as a solid, a liquid, and a vapour; 5th, the small quantity required, and hence its portability.

"I recommend that a bottle of the acid or tin of the powder be kept in every privy or water closet, so that a little may be thrown down by each person using it; by this plan all offensive smell will be prevented. I may just add, that I find it extremely useful in contagious dysentery and typhoid fever, to disinfect the evacuations."

In a report made by Dr. Trench, the medical officer of health for Liverpool, in December, 1869, he remarks, "There need be no controversy as to the comparative value of the different disinfectants, such as sulphate of iron, sulphate of zinc, chloride of lime, permanganate of potash, quicklime, charcoal powder, carbolic acid. They all have their special modes of action, and each may be occasionally the very best to be employed.

"In choosing carbolic acid as a disinfectant, I am influenced by its price and its efficiency. 1. It is a positive disinfectant, and quickly destroys or restrains every contagious and infectious virus. 2. It is an antiseptic, and arrests and prevents fermentation and decay. 3. It is used with facility, and is sufficiently volatile to permit its vapour to reach atoms or germs of disease floating in the air. 4. It is cheaper than chloride of lime, and for out-door disinfection, as well as the disinfection of privies and drains, it is more permanently efficacious."

Messrs F. C. Calvert & Co., the manufacturers of this product, give the following directions as to its use:—

"Directions for the use of Carbolic Acid Crystals.—The crystallized carbolic acid is soluble in water, and *one pound to every five gallons of water* is sufficient for deodorizing and disinfecting purposes.

"The bottles, when opened, should be placed in the water for about one hour (according to the temperature), 4, 8, or 12 of the bottles, which each contain a pound, being used for a tank of either 20, 40, or 60 gallons. The bottles should be cleared of all adhering crystals, and the solution well stirred previous to use.

"A solution of this strength is applicable for deodorizing of sinks, water closets, or wherever bad odours exist, and being neither alkaline, acid, nor corrosive, no injury need be apprehended to wood, iron, metal, or clothes. In a concentrated form the acid acts as a caustic, but its action on the skin may readily be arrested by rubbing with sweet oil.

"*For hospital wards, night asylums, &c.*—To keep them in a healthy state, and to prevent any spread of contagious diseases, dissolve 1 lb. of crystallized carbolic acid in 30 gallons of water, and sprinkle the floors with the solution, which may also be employed for deodorizing the chamber utensils.

"The solution may be used in *fœtid ulcers, cancers, gangrenous and all offensive sores*; it removes all disagreeable smell and putrescency, and renders the discharge innocuous to the contiguous living and unaffected tissues. In its diluted state, therefore, it is a great boon to patients labouring under that class of disease.

"*When small-pox, typhoid fevers, &c.*, occur, the spread of contagion may be prevented by proper use of this disinfectant. In such cases the acid should be used in the crystalline form, viz., 1 lb. of the crystals to 5 or more lbs. of wet sand, placed in shallow vessels in various parts of the sick room.

"In case of any epidemic breaking out in a house, the same mixture should be used as a sanitary precaution *throughout the same.*

"*Infected clothing and bed linen* can be thoroughly purified and rendered fit for use, if well washed in the aqueous solution."

The liquid acid may be used in a similar manner. The disinfecting powder supplied by them contains fifteen per cent. of carbolic acid and cresyl alcohol, and is employed as follows:—

"*For sick rooms.*—Placed in dishes about the room, this powder gives off carbolic acid freely; it must be renewed once in twenty-four hours. Infected clothing and bed linen can be purified and made fit for use, if well washed in water into which $\frac{1}{4}$ lb. powder has been mixed with each bucket-full.

"*As a disinfectant.*—The powder may be used by mixing one lb. in a bucket of water; or by sprinkling it lightly over the surface to be disinfected.

"*For dead bodies.*—Spread over the bottom of the coffin 2 lbs. of the powder before putting the body in; then dip a sheet in a solution of the powder (1 lb. to a gallon of water) and cover the body with it; this will prevent any effluvia or disease being disseminated therefrom."

Carbolic acid is also used in the form of vapour for purifying the atmosphere of hospital wards, and other places where contagious diseases exist. Half an ounce of acid is sufficient for an ordinary sized sick room.

A very convenient form of vaporizer is one designed by R. Le Neve Foster, F.C.S., Figs. 2 and 3.

"The iron heater A is to be placed in a fire until it has the required temperature, when it is to be removed

Fig 2.

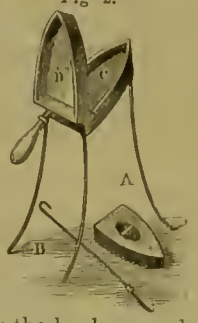



Fig. 3.



by the hook, B, and placed in the box, C; the lid D must then be closed.

"The carbolic acid is then poured into the enamelled dish above the lid, and in a few minutes the carbolic vapours will be given off and diffused throughout the atmosphere of the place to be fumigated."

The following is the method of disinfection carried out in Bristol by Dr. Davies, the medical officer of health, as described by him.

"The city is divided into four districts; each district has an inspector in it—there is also a superintendent inspector; each district inspector in the summer time has two workmen at his command, and one in winter, to white-lime dirty walls, courts, and alleys, to let off foul ejects in privies, &c. They carry with them a bucket of Calvert's powder, which they sprinkle over the pans, &c., of the closets, over every street grating, and every eject they pass. When we suspect any division of the sewers to have the germs of disease in it, we throw in a considerable quantity of sulphate of iron and of liquid carbolic acid.

"I meet the district inspectors daily at 11 a.m., and if they report any disease of a zymotic character among the poor, I visit the affected persons, and order the floor to be thickly sprinkled with carbolic disinfecting powder. I supply the friends with it gratuitously, and order them to keep the chamber utensils always charged with it. If the patient dies, we supply some to be sprinkled over the corpse.

"Being a strong believer in the germinal origin of all zymotic disease, I have followed this plan with unwavering firmness, and I can only say that our success here has been very extraordinary, as testified by our death rate. Houses affected with zymotic disease we treat, after the removal of the patient, under the 22nd section of the Sanitary Act, 1866.

"In one or two minor matters I differ with other reporters. The powder, if fresh, is not innocuous to the hands; our workmen used to sprinkle it with their hands, but were obliged to desist on account of its irritating the skin—they now use small hand ladles.

"If sprinkled over French-polished furniture it spots them; it does not hurt metals, boards, or clothing; it never produces irritation of the lungs, though some persons dislike it, and complain of nausea when exposed to it."

Carbolic acid soaps are another form of using this valuable antiseptic.

Salicylic acid is allied to carbolic acid, and possesses exceedingly valuable antiseptic properties. It is made in the form of a powder, devoid of smell, and is soluble in about 300 parts of water.

Salicylic acid has not yet been produced on a sufficiently commercial scale to come into use as a general disinfectant, though many experimental tests have shown that for some purposes it surpasses carbolic acid.

*Chlorine, Chlorides of Zinc, Lime, and Aluminium.*—Of these, chlorine doubtless holds the foremost place. Chlorine is prepared by heating a mixture of black oxide of manganese with hydrochloric acid.

Fig 4 is a representation of an ingenious and simple contrivance for liberating chlorine.

Having introduced the binoxide of manganese into the glass basin B, put on the perforated wooden cover, C, fix the globular vessel, A, in the orifice, and pour a quantity of hydrochloric acid into it; then

Fig. 4.




turn the stopper, *a*, and allow about a table-spoonful of acid to drop from the globe, upon which the gas will be set free, emanating through the holes in C.

When a further supply of chlorine is needed, it is merely required to again turn the stopper, and allow more acid to pass into the basin.

Chlorine is extremely irritating, and cannot be used with safety in the sick chamber, as the quantity required to disinfect the room efficiently would be irrespirable. It has, however, proved useful for fumigating houses where epidemics have existed.

Chloride of zinc and the other metallic chlorides absorb ammonia and sulphuretted hydrogen, and are useful as disinfectants of fœcal matter. In the report of the Royal Cattle Plague Commission, 1866, Mr. W. Crookes, F.R.S., states, with regard to them, that "they possess no power to destroy specific infective emanations," and that chloride of lime is "very irritating to the lungs of diseased and convalescent animals."

For the disinfection of textile fabrics they are too corrosive, and being usually acid, destroy it.

Chloride of zinc, in the proportion of 1 part to 300 of water, instantly destroys infusorial life, and when diluted to but 1 part in 1000 of inorganic liquid, will check decomposition for a considerable time.

As aerial disinfectants, the chlorides possess little or no power.

*Sulphurous Acid and the Sulphites.*—Sulphurous acid has been used from time immemorial as a disinfectant. It is easily prepared by burning sulphur in the air. It has a powerful odour, and even when present in the air in the proportion of 20 parts to 100,000 parts of air, it is irritating to the system; and 4 parts in 10,000 of air render the air irrespirable. A much smaller proportion present is sufficient to destroy vegetable life.

Water absorbs from 40 to 50 times its own bulk of sulphurous acid, and forms with it a powerful disinfectant.

Owing to its irritating property it is impossible to use it as an aerial disinfectant in sick rooms.

The sulphites possess in a marked degree the properties of sulphurous acid.

The metallic sulphates are useful disinfectants, but are useless as aerial disinfectants, being non-volatile.

A solution of 1 part of a metallic sulphate in 250 parts of an organic solution will prevent the manifestation of infusorial life.

One pound dissolved in a gallon of water is a good disinfectant for drains and fœcal matter.

*Permanganate of potash* is an oxidizing agent, and does not appear to exert much action on vital manifestation, but is active in the destruction of dead organic matter. This property renders it valuable as a means of purifying potable water. It is of no value as an aerial disinfectant.

*Charcoal* is a powerful disinfectant, and owes its action to its property of condensing upon its surface and within its pores large quantities of vaporous and gaseous matter, which, by the very force of condensation, they bring into contact with the oxygen of the atmosphere, and thus burn up organic miasms by a process of slow combustion. Wood charcoal will absorb about 9 times its volume of oxygen and 90 times its volume of ammonia.

Dr. Stenhouse in 1853 performed a series of experiments, tending to show the relative value of wood, peat, and animal charcoal. Half a gramme of each kind absorbed the undermentioned number of centimètres of different gases:—

| Kind of charcoal. | Ammonia. | Hydrochloric acid. | Sulphide of hydrogen. | Carbonic acid. | Oxygen. | Sulphurous acid. |
|---|---|---|---|---|---|---|
| Wood,.. | 98·5 | 45·0 | 30·0 | 14·0 | 0·8 | 32·5 |
| Peat,... | 96·0 | 60·0 | 28·5 | 10·0 | 0·6 | 27·5 |
| Animal,. | 43·5 | — | 9·0 | 5·0 | 0 5 | 17·5 |

It thus appears that wood charcoal possesses the

highest absorbent power for ammonia, sulphide of hydrogen, and sulphurous acid; while animal charcoal is decidedly inferior to those of wood and peat as an *absorber* of gases.

Dr. Stenhouse availed himself of the absorbent property of charcoal in the construction of a respirator which became a sanitary instrument of great value. It consisted, as first constructed, of a hollow case made of fine flexible wire-gauze, about half an inch wide internally, and of sufficient length and breadth, when folded over the lower part of the face, to cover closely either the mouth alone, or if required the lower part of the nose also. The hollow space is filled with coarsely powdered charcoal, and the whole, like the metallic respirator, is fitted to the face and fastened over the head by attachments of ribbon. All the air that enters the lungs must pass through this charcoal sieve, and is thus deprived of the noxious vapours or gases it may contain. After some time the charcoal powder becomes saturated, or too old to act with efficiency, but an ounce of powdered wood charcoal renews it, and the instrument is itself again. Dr. Stenhouse has also shown that platinized charcoal has a still greater power of oxidation. The form of the respirator has since been materially altered and also reduced in size.

Charcoal is employed largely for water filters, which, with water containing free oxygen or worked intermittently, will purify water from the foulest matters.

Dr. Letheby has adopted charcoal filters in the ventilating shafts of the sewers of the city of London. They consist of an iron box, 18 inches deep and 14 inches square, containing a movable frame of six trays or sieves, upon each of which there is a layer of wood charcoal in pieces as large as filberts, and 2 inches deep. After seven years' experience he reports their working as a perfect success.

*Disinfecting Stoves.*—The following is a description of the disinfecting apparatus in use in Liverpool designed by the late borough engineer, Mr. Newlands, and shown on Disinfectants, Plate I:—

"*a*, court-yard; *b*, keeper's cottage; *c*, yard to cottage; *d*, receiving house for infected clothes; *e*, depository for clothes after they are disinfected; *f*, wash-house; *g*, drying closet; *h*, disinfecting stoves; *i*, boiler; *j*, stoke hole; *k*, heating apparatus; *l*, coals; *m*, ashes; *n*, cold air shaft; *o*, cold air flue; *p*, hot air chamber; *q*, exhaust flue; *r*, chimney shaft; *s*, cistern.

"The plot of land on which the buildings are erected is situate in New Bird Street, with a frontage thereto of 56 feet, and extending backwards to the depth of about 70 feet. They comprise a spacious flagged court-yard, with paved cart way, a residence for the keeper, a well ventilated receiving room for infected clothes, a depository for disinfected clothes, a wash-house for cleansing infected clothing (containing eight washing troughs, supplied by steam from the boiler in the basement), a drying closet opening directly into the wash-house, and a range of disinfecting chambers under the open shed in the court-yard.

"In the basement are the boiler, stoking pit, heating apparatus, and the coal and ash vaults.

"The disinfecting stoves are each 5 feet wide, 7 feet from front to back, and 6 feet 6 inches high to the springing of the arch.

"The walls and vault are built of brickwork, the doors are of wrought iron, fitting tightly into cast-iron frames.

"The floors are formed with double iron gratings, having alternate openings, the under one being constructed so as to slide, to exclude, if desired, the hot air.

"In the arch over the centre of each stove is an opening, containing an iron valve for the escape of foul air into an exhaust flue, which is carried over the top of the stoves into the chimney shaft.

"Within the thickness of the front wall of each stove a thermometer is fixed, protected from contact with the outer air by a thick plate of glass.

"The drying closet in the wash-house is of a similar construction, with the addition of light wrought-iron sliding clothes' horses.

"The heating apparatus is a cast-iron cockle, patented and manufactured by Messrs. Tessimond & Kissack. Two cast-iron smoke-tight flues are connected therewith, which, after forming a coil, are conveyed along the hot chamber under the stoves into the chimney at the opposite end.

"The furnace doors and ash hole are each regulated by means of sliding dampers.

"Cold air is drawn from the atmosphere through a descending shaft, thence along a brick flue, underneath the floors of the stoke hole into a cavity on each side of the cockle, after passing which it is highly heated and conveyed into a chamber extending underneath the whole length of the stoves and drying closet, and from which it is admitted into the stoves through the sliding gratings before mentioned.

"The temperature of the air is regulated by means of a damper at the entrance to the cold-air flue. As many as 380° Fahr. have been registered in the drying closet over the cockle, and 280° in the stoves."

Dr. Trench, the medical officer of health for Liverpool, says they could raise the temperature as high as 500° Fahr.; but that from experience they find that some fabrics are scorched and injured if kept in the chamber for any length of time at any heat above 212° Fahr. He also adds, that in addition to heat, carbolic acid powder is freely sprinkled on the floor of the chamber, so that the vapours reach the articles in the chambers.

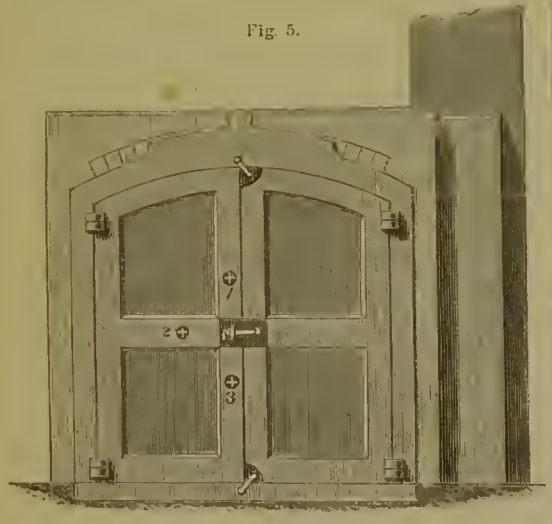
The disinfecting stove used in the Royal Victoria Yard, Deptford, consists of a brick chamber with a slightly arched roof, and an iron movable floor in two pieces. The chamber is 7 feet deep, 6 feet 9 inches wide, and 5 feet 8½ inches high in the centre of the arch. It is heated by a flue below the iron floor passing round three sides of the chamber and up a chimney. There is an opening in the upper part of the chamber in its centre which passes along

in the roof to the side, from thence down in the wall entering beneath the fire; this carries any of the foul air of the clothes from the chamber through the fire and up the flue. This proceeding takes place after the clothes have been in the chamber say an hour and a half in the following manner:—The damper in the foul-air shaft is withdrawn and the furnace door is shut; any draught that gets to the fire comes from the chamber. Over the opening into the furnace is a square opening, fitted with a glass, inside of which is a fixed thermometer. When this shows a temperature of 200° Fahr. the interior of the chamber is at 250° Fahr., the highest point at which it is allowed to be. In the interior of the chamber, at the sides, there are little movable cranes, three rows of three supporting rods of iron on which wooden trays rest, and on which the clothes are placed when the iron cart is not used. The cranes move fore and aft to be out of the way when the cart is used. The cart is of iron on wheels, and runs into the chamber on tramways to keep it in position; in the interior of the cart are three iron trays for laying the clothes on. The lowest tray is always the hottest, so that it is prudent to use the cart, the iron bottom of which prevents burning. The iron ends of the cart are removed when it is placed in the chamber, so is the handle. It is usual to keep the clothes at the temperature of 250° Fahr. for two hours.

There is a trap door 8 inches square about 14 inches above the upper edge of the furnace, and on a level with the iron floor of the chamber, for disinfectants. Carbolic acid and sulphur are used; the former is placed on a flat plate, the latter is sprinkled over the floor. These are used at the last, and after that has been done the clothes are fit to be used without danger to any one.

*Elevation plan* (Fig. 5) shows the front of the chamber with the doors closed; the openings Nos. 1,

Fig. 5.

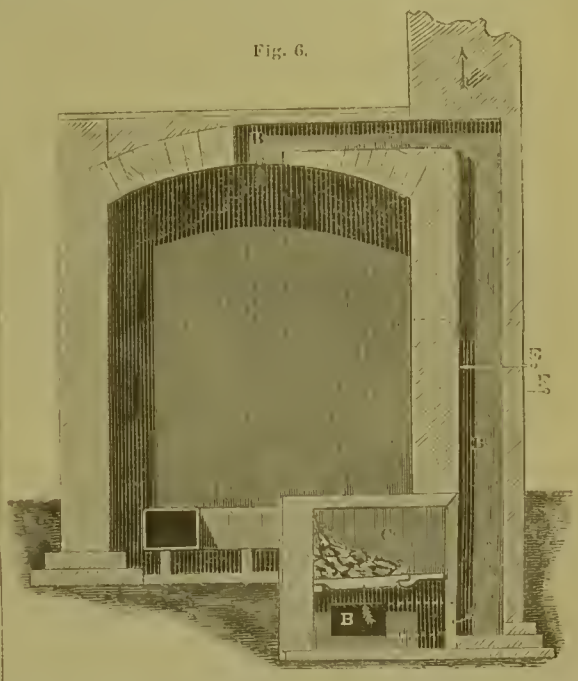



2, and 3 are for inserting the long thermometer, which is pushed into the clothing to be disinfected; they correspond with the three trays.

The thermometer can be withdrawn and examined without allowing much cold air to enter; plugs fit into these three openings when not used for the thermometer.

*Section* (Fig. 6).—The chamber is shown about the centre of its depth; the foul-air shaft B passes along the roof down the side wall and beneath the fire, C; the

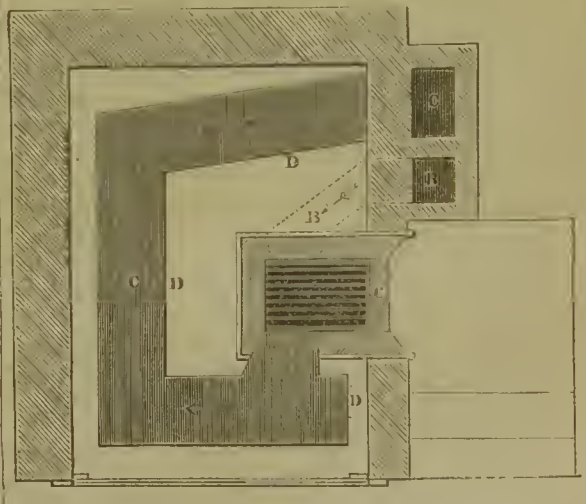
Fig. 6.




opening where the fixed thermometer is placed is marked with dotted lines. The damper for the foul-air shaft, E, is represented as shut, and the damper for the chimney, F, is also shut.

The *Ground Plan* (Fig. 7) shows the flue beneath the iron plates which form the floor of the chamber,

Fig. 7.




the dotted lines showing the foul air flue, B, as it passes beneath the fire. In the flue, C, there are openings at D D D for the purpose of cleaning it.

**DYEING AND CALICO PRINTING.—Chemistry of Dyeing and Printing.**

*General Introduction.*—The object of the various processes which are used in dyeing and printing is to impart to a textile fabric a certain colour, and to fix it in such a manner as to make it insoluble in water, and thus prevent it from being removed by washing. This fixation is chiefly effected by chemical reactions, which vary greatly with the nature of the fibre, as well as with that of the colouring matter. In some cases the operations are very simple, and in others highly complicated, several chemical processes taking place either simultaneously or successively.

The animal and vegetable tissues which are used for dyeing differ in their chemical composition as well as in their properties. The principal vegetable fibres are *cotton* and *linen*. In the pure state they consist of a compound called *cellulose*, $C_6H_{10}O_5$, which forms a large proportion of the solid parts of all plants. The pure substance is easily obtained by treating cotton or fine linen with a dilute alkali, dilute acids and ether, which remove all adhering impurities. It is insoluble in water and alcohol, but readily dissolves in an ammoniacal solution of copper oxide (SCHWEITZER'S reagent); on adding an acid to this solution cellulose is precipitated as a white amorphous mass. The cellulose of different plants can be easily distinguished by the microscope, each exhibiting a peculiar structure.

*Cotton* is the product of different species of *Gossypium* growing in warm countries. The fruit of these plants is a large capsule containing a mass of fine long fibres which envelop the seeds. The microscopic study of cotton is of great interest, offering not only the key to the theory of the fixation of colours, but also the means of distinguishing it from other fibres. According to the late WALTER CRUM, F.R.S., mature cotton fibre consists of a hollow, shrivelled, irregularly-twisted cylinder, of about $\frac{1}{1000}$th of an inch at its greatest diameter; and if we take middling Orleans at $1\frac{1}{4}$ inch long, a cord of $\frac{1}{8}$ inch diameter and 13 feet long would give an idea of its relative dimensions. It is, however, not of equal thickness. Towards the end farthest from the seed it gradually diminishes, like the tape-worm, to about one-fifth of its greatest diameter, and there its form is more nearly cylindrical and straight. The walls of these tubes do not exhibit openings of any kind which can be taken for lateral passages; but it cannot be doubted that, like other ligneous matter, they are pervious to fluids.

In order to dye cotton the substance to be employed must be in a state of solution, so as to enter the fibre or pass through its pores, and be there made insoluble or precipitated by chemical means. Thus the colour is entrapped within the fibre or its tissue, and becomes fixed there. This is proved by the fact, that on unripe cotton fibre, or *dead* cotton, as it has been called, no colour can be fixed. The unripe fibre consists of very thin and remarkably transparent blades, which are readily distinguishable from those of mature cotton by their perfect flatness, not having the vestige of a cavity even at the sides, being perfectly flat, and broader than the usual fibre.

Strong caustic alkali has a very peculiar effect on cotton. The fibre contracts in length, becomes almost circular, and the cavity shrinks considerably. MERCER has shown that cotton thus treated is stronger, and has a superior attraction for colours, and it was at one time believed that this process, which is called "Mercerising," would yield great results; but unfortunately it has not turned out so useful as was expected, the objections being the large expense of the soda and the great contraction of the fibre, which although making the cloth look finer, is an effect which is more cheaply produced by weaving.

Dr. SCHUNCK has found that cotton in the raw state, as furnished by commerce, contains besides cellulose a certain number of other substances, some of which occur so constantly that they may be considered essential constituents of cotton viewed as a vegetable product. The object of the bleaching process, to which most cotton fabrics are subjected, is to deprive them of the impurities which are either natural to the fibre itself, or have been introduced accidentally or designedly during the process of manufacture. Notwithstanding the importance of an accurate knowledge of everything connected with this staple, from an industrial point of view, the substances existing in cotton fibre have never before the researches of SCHUNCK been subjected to a special chemical examination.

According to PERSOZ the tissues of cotton, hemp, and linen contain: —

1. A certain quantity of colouring matter, which is more or less protected by the bodies which accompany it, naturally or accidentally.

2. A peculiar resin, insoluble in water, and not easily soluble in alkalies, which plays the part of a resist, and protects the colouring matter inherent to the fibre from the action of the agents which are employed to destroy and remove it.

3. A certain quantity of fatty matter, a very small portion of which is inherent to the fibre, the greatest part being derived from the operations of spinning and weaving.

4. A neutral substance, which consists either of flour, starch, or glue, according as the one or the other has been employed in sizing the warp before weaving.

5. Inorganic salts, some of which are peculiar to the fibre, while the others are derived from the water and the matter used in dressing the warp.

Dr. R. A. SMITH says that the substances present in cotton goods, and to be treated in bleaching, are as follows:—*a*, The resinous matter natural to the filaments; *b*, the colouring matter of the plant; *c*, the paste of the weaver; *d*, a fatty matter; *e*, a cupreous soap; *f*, a calcareous soap; *g*, the filth of the hands; *h*, iron rust, earthy matters, and dust; *i*, the cotton fibre itself; *k*, the seed vessels.

The object of the subsequent research of Dr. SCHUNCK was to throw a little more light on the nature of the substances which are contained in or

attached to the framework of the cellulose of which cotton fibre mainly consists, and which are, together with the latter, produced by the plant, without taking into consideration the foreign and extraneous matters introduced during the process of manufacture. It is well known that these substances are almost insoluble in water, but soluble in hot alkaline lye. Indeed the principal operation in the bleaching of cotton goods consists in subjecting them for some time to the action of boiling solutions of soda or some other alkali, chlorine or its compounds being only used to impart to them the highest degree of whiteness.

Schunck did not use raw cotton, but cotton-yarn made from definite unmixed kinds of cotton; because it is much freer from mechanical impurities, which are to a great extent removed during, or rather previously to, the operations of spinning; while, on the other hand, in a well-ordered manufactory little or nothing of a foreign nature is added to the cotton to make it impure. Another advantage is, that it is less bulky, and can be more easily worked in such quantities as were required for this investigation. The yarn was exhausted with a solution of soda-ash, and the dark-brown solution precipitated by an acid. The brown precipitate thus obtained from different kinds of cotton amounted to—

| | Per cent. |
|---|---|
| Dhollerah, | 0·337 |
| Middling Orleans, | 0·480 |

On burning it left 2·3 to 6·9 per cent. of ash, consisting of oxide of iron, alumina, silicate of alumina, sulphate of soda, and sulphate of lime. The other substances present are—

1. *Cotton wax.*—A body having in its physical and chemical properties, and its composition, the greatest resemblance to vegetable waxes, such as carnauba wax. The cotton wax is undoubtedly identical with Persoz's resin.

2. *Solid fatty acids*, most probably a mixture of palmitic and stearic acids.

3. A colouring matter, easily soluble in alcohol.

4. A colouring matter, sparingly soluble in alcohol. These two colouring matters exist in all kinds of raw cotton; "nankin" cotton differing from white cotton only by containing much more of these colours.

5. *Pectic acid.*

6. *Albuminous matter.*

*Linen* consists of the fibres of flax and hemp. Under the microscope they appear to be hollow cylinders, which are open at both ends, and provided with knots, which are distributed irregularly over the surface.

*Hemp* is much coarser than linen, the fibre of the former having a diameter of $\frac{1}{500}$ to $\frac{1}{750}$th of an inch, and that of the latter, $\frac{1}{1000}$ to $\frac{1}{1500}$th of an inch. Linen does not take up colours so readily as cotton, but its attraction for colouring matters is also increased by mercerising.

The most important animal fibres are *wool* and *silk;* both differ from vegetable fibres by containing nitrogen, besides carbon, hydrogen, and oxygen.

*Wool* has, when purified from the greasy matters and suint, which it naturally contains, the same composition as the so-called albuminous substances, which are such complicated compounds that it has not been possible to assign to them a definite formula. Wool also contains about 2 to 3·5 per cent. of sulphur. The fibre of wool consists of very elastic cylinders, which are covered with scales, and have a diameter of about $\frac{1}{600}$ to $\frac{1}{1600}$th of an inch. Wool readily dissolves in caustic alkalies, and in hot ammoniacal solution of copper oxide, but is not acted upon by the cold liquid. Dilute nitric acid and picric acid impart to it an intensely yellow colour.

*Silk.*—Raw silk contains naturally a large quantity of gummy substances, which are removed by *scouring* or boiling the silk in soap and water. Silk is the longest fibre known; the thread often exceeds a length of 1300 feet, but having only a diameter of about $\frac{1}{2000}$th of an inch. Under the microscope it appears as a cylindrical fibre, not showing any distinct structure.

It readily dissolves in alkalies, and in a cold solution of an ammoniacal solution of copper oxide. Dilute nitric acid and picric acid colour it yellow.

When raw silk is heated with water under pressure, it yields two distinct compounds, viz.:—

*a*, *Fibroïn*, $C_{15}H_{23}N_5O_6$, in quantity equal to 66 per cent.; it is a silky glistening substance.

*b*, *Sericin* or *Silk-gelatin*, $C_{15}H_{25}N_5O_8$, a body resembling gelatin. From its hot aqueous solution it is precipitated by alcohol as a colourless powder, which forms a transparent jelly with cold water.

The fibres of cotton, linen, wool, and silk can be easily distinguished from each other, and detected when they are mixed, by means of the microscope or by the help of chemical reagents.

The appearance of the fibres under the microscope has already been described. If a mixed fabric containing vegetable and animal fibres be treated with strong hot caustic soda, the latter only will dissolve, whilst by the action of dilute nitric acid or a solution of picric acid, and subsequent washing, the vegetable fibres will remain perfectly colourless, and the animal fibre be dyed a permanent yellow. When silk or wool is treated with a hot solution of mercuric nitrate, they take a red colour, while cotton or linen remains white. The latter are strongly attacked and become rotten if moistened with weak hydrochloric acid and dried, while wool and silk remain unchanged. Another very characteristic reaction of wool is, that on moistening it with a solution of lead oxide in caustic soda it blackens, on account of the sulphur contained in it.

Silk is not blackened by an alkaline solution of lead, and is completely soluble in a cold neutral solution of zinc chloride, which does not dissolve wool.

As a general rule animal fibres have a much stronger attraction for colours than vegetable fibres; they take up the colours more readily and hold them more firmly. Not only colouring matters but other substances also are taken up from a solution by the different fibres; such are the different tannic acids and similar substances which are used in dyeing.

The question has often been discussed whether the fibres combine chemically with the colouring matter or not. There is no doubt that a fibre cannot take up more than a certain quantity of a certain colour; but it has never been shown, and it is also very improbable, that a fibre combines with colours in definite atomic proportions, as is the case in true chemical compounds. Moreover, neither the colours nor the fibres lose, in combining, any of their distinct and characteristic properties; and consequently it is possible to remove a colour from a dyed fabric by suitable solvents, and thus obtain the fibre again in its original state.

The great advocate of the chemical theory was the late MICHEL E. CHEVREUL, while WALTER CRUM always maintained that the fixation of all colours was only an attraction of surface resembling that which animal charcoal and other porous bodies exert on colouring matters. At that time the coal-tar colours were not known: these compounds possess the characteristic property of dyeing with the greatest ease, not only all animal fibres, but also bodies having a similar composition, such as skin, albumen, and so on, while they cannot be combined directly with vegetable fibres. From this it would appear, that in dyeing both a chemical and a mechanical action may come into play.

The organic fibres possess also the property of precipitating certain salts or metallic oxides within their tissue. Thus, if cotton be passed through a solution of ferric nitrate, it fixes some oxide of iron, and from an alkaline solution of alum it absorbs the excess of alumina; silk does the same, but its attraction for oxides is much greater, and by passing it repeatedly through a solution of iron or tin salts, and taking care to remove the acid which is set free, a very large quantity of the oxides of these metals may be incorporated into silk. Wool acts in a similar way, and absorbs alum, potassium dichromate, and other salts from their solution.

The different colours which are used in dyeing and printing may be conveniently divided into the following groups:—

I. *Substantive Colours.*—The colours forming this group have the property of combining readily and directly with animal fibre, as well as with substances having a similar composition, such as albumen, casein, skin, hair, &c., but only a few dye directly cotton or linen, and generally produce only very faint shades (*tint shades*); in this case the absorption of the colour is certainly only due to a mere attraction of surface, which is quite similar to that by which certain precipitates, as calcium carbonate, barium sulphate, &c., carry down colouring matters from a solution. However, almost all substantive colours may be fixed on cotton by means of *mordants*, *i.e.* bodies forming with the colour an insoluble compound, which is precipitated within the fibre. Silk and wool are themselves mordants, or perhaps more probably contain compounds acting as mordants.

II. *Adjective Colours.*—These bodies are like those of the first group, coloured compounds, but differ from them by not being absorbed by animal or vegetable fibres, and therefore dye only by the intervention of a mordant.

III. *Mineral and Pigment Colours.*—These colours are insoluble in water and spirits of wine, and are either precipitated within the tissue by various chemical reactions, or simply fixed by mechanical means. The following list contains a short description of all the more important colouring matters which are employed for dyeing and printing:—

SUBSTANTIVE COLOURS are divided into two groups: (*a*) Such as exist ready formed in nature, and occur chiefly in plants. The most important of these colouring matters are *indigo*, *archil*, *safflower*, and *annotto*. (*b*) Artificial or coal-tar colours.

*Natural Substantive Colours.*—*Indigo*, which is one of the most valuable dye-stuffs, is the product of a great number of plants, the most important being different species of *Indigofera*, which belong to the family of *Papilionaceæ*, or the pea family, and are indigenous to India and China, but also grow abundantly in Africa, West Indies, and South America, and are cultivated in all countries where the soil and the climate allow it. The most important are *I. tinctoria*, *I. anil*, *I. argentea*, and *I. disperma*. They grow to a height of 3 to 5 feet, and have a single stem, which ramifies at the upper end and bears pinnate bluish-green leaves.

The round black seeds are sown in India in March or April in a light soil, and the plants are cut or mown towards the end of June or in July, as soon as the first flowers appear. A second and third crop is obtained, but their yield of indigo is less. Of other indigo plants may be mentioned *woad*, or *Isatis tinctoria*, a biennial plant belonging to the cabbage family, or *Cruciferæ*, and growing in Middle Europe; *Polygonum tinctorium*, a native of China; *Marsdenia tinctoria*, *Nerium tinctorium*, *Justicia tinctoria*, and *Asclepias tingens*.

None of these plants contains the colouring matter in the free state, but as a peculiar compound, which SCHUNCK, who first isolated it, has called *Indican*. It is a brown syrupy mass, having a nauseous and bitter taste. By the action of dilute mineral acids it is resolved into *indigotin*, a kind of sugar called *indiglucin*, and other products.

The composition of indican is, according to Dr. SCHUNCK, expressed by the formula $C_{52}H_{62}N_2O_{31}$; and when it is decomposed it is principally resolved into indigo blue and indiglucin, according to the following equation:—

$$C_{52}H_{62}N_2O_{31} + 4H_2O = \overset{\text{Indigotin.}}{C_{16}H_{10}N_2O_2} + 6\,\overset{\text{Indiglucin.}}{C_6H_{12}O_6}.$$

Besides the chief products, other bodies are formed: *carbonic acid* escapes, *leucine*, *tyrosine*, and *fatty acids* remain in solution, and *indifuscin*, *indihumin*, *indiretin*, *indifulvin*, and *indirubin*, are precipitated with the indigo blue.

*Indigotin*, or indigo blue, $C_{16}H_{10}N_2O_2$, forms the blue colouring matter of indigo, which is obtained by macerating the plants with water and a little lime, exposing the liquid in flat vessels to the air, and stirring it up frequently. In the place of lime,

ammonia is now used in Java, which is said to give a purer colour. A fermentation soon sets in, by which the indican is decomposed and indigo separates out as a blue powder, which is boiled with water in order to remove a yellow colouring matter, and then pressed and dried. Indigo is found in the market in cubic cakes or in round masses, "fig indigo," which, when rubbed with a hard body, exhibits a copper-red lustre.

Indigo is a mixture of different bodies, containing, besides indigotin, the brown and red colouring matters which have already been mentioned, and inorganic bodies, which on burning are left behind as ash.

According to LEUCHS a certain relation exists between the specific gravity of indigo and the quantity of indigotin contained in it. The more colouring matter it contains the lighter it is, and the determination of its specific gravity may therefore be used as a test for its value. This will be seen from the following table:—

| Percentage of indigotin | Specific gravity. |
|---|---|
| 56 56·5 | 1·324 |
| 55 | 1·332 |
| 53 | 1·350 |
| 49 | 1·371 |
| 44 | 1·384 |
| 40 | 1·421 |
| 37 | 1·437 |
| 30·5 | 1·455 |

This difference in the specific gravities is undoubtedly due to the varying quantities of inorganic matter contained in the different samples, and it has therefore been proposed to test the value of indigo by determining the amount of ash contained in it.

To obtain pure indigotin, indigo is finely powdered and put together with grape sugar and strong soda-lye into a flask, which is completely filled with hot alcohol and well corked. After standing for some time a yellow, clear solution is formed, containing *indigo white* or *hydrindigotin*, $C_{16}H_{12}N_2O_2$, which on adding an acid is precipitated, but in contact with air quickly oxidizes to indigo blue. When the alkaline liquid is exposed to the air it also absorbs oxygen, and indigotin is precipitated. In the place of grape sugar and alcohol, ferrous sulphate and hot water may be used, and the soda may be replaced by lime or any other alkali. As the value of indigo depends only on the amount of indigotin contained in it, this reaction offers a ready means for determining this. JOHN DALE, who has examined this subject very carefully, has found that in this reaction a certain quantity of indigotin undergoes such a change that it is not reprecipitated, and this of course has to be taken into account. His method for testing indigo is the following:—

75 grains of finely powdered indigo are heated with 1 dram of caustic soda of 60° TWADDLE and 5 oz. of water just to the boiling point, and then thrown on a small calico filter and washed with a little water. The filter is then tied up to form a small bag, which is rubbed between the hands in water until the colour is all out of it. 200 grains of ferrous sulphate dissolved in water and 200 grains of freshly-slaked lime are now added, and the whole is made up to 3 quarts, and after being thoroughly mixed a Winchester quart bottle is completely filled with it and tied over with bladder. This must be done with great care, so as to leave no air-bubble in the bottle, which is repeatedly shaken for 12 hours, or better 2 or 3 days, and then allowed to stand until the liquid is quite clear. The bladder is now sliced, and by means of a charged syphon 1 quart is drawn into a measured vessel. To this 1 oz. of acetic acid is added and the whole well stirred. When all the indigotin has separated out, it is collected on a tared filter, washed with warm water, and weighed after drying at 100° C. The weight found multiplied by 4 gives the percentage, to which 4 grains must be added.

Indigotin has a deep blue colour, with a purple tinge, and is insoluble in water, dilute acids, and alkalies; but it dissolves in boiling aniline with a deep blue colour, and in hot paraffin with a purple colour. On cooling these solutions indigotin separates out in small crystals. It is also slightly soluble in boiling alcohol and ether. When indigotin is heated to 300° C. it forms a purple vapour, which condenses in prisms having a purple lustre. When indigotin is treated with oxidizing agents it is converted into *isatin*, $C_{16}H_{10}N_2O_4$, which forms orange crystals.

Indigotin or indigo dissolves in highly concentrated sulphuric acid with a deep blue colour—the first product which is formed being *indigo-monosulphonic* or *indigo-purpuric acid*, $C_{16}H_9N_2O_2(SO_3H)$, which by the further action of sulphuric acid is converted into *indigo-disulphonic* or *indigo-sulphuric acid*, $C_{16}H_8N_2O_2(SO_3H)_2$; generally both are present together in the solution, and can be easily separated by adding water, which precipitates the first of these acids, while the second remains in solution.

*Indigo-purpuric acid* is almost insoluble in dilute acids, but dissolves in water with a blue colour. With alkalies it forms purple salts, which are sparingly soluble in water. The sodium salt is used for dyeing, and is called *red indigo-carmine* or *indigo-purple*.

*Indigo-sulphuric acid* forms blue salts. The sodium salt is an amorphous mass, which is known in commerce by the names of *indigo-extract* or *indigo-carmine*.

Indigo-sulphuric acid is converted by oxidizing agents into *isatin-sulphuric* or *isatin-sulphonic acid*, $C_{16}H_8N_2O_4(SO_3H)_2$, which has an orange colour. This reaction may also be used for determining the percentage of indigotin in indigo. The best method, among the many which have been proposed, appears to be that of E. SCHLUMBERGER.

One gramme of indigo is very finely powdered and dissolved at a very gentle heat in 12 grms. of Nordhausen sulphuric acid. All the indigotin is dissolved, while the other organic matters are carbonized. The solution is diluted with water, filtered, and made up to 1 litre. To 100 c.c. of this solution 10 c.c. of hydrochloric acid are added, and the liquid is heated until it begins to boil. Then, by means of a burette, a solution of potassium dichromate containing 7·65

grains in a litre is added until the liquid, which first assumes a greenish colour, changes into a pure orange. Each c.c. of the chrome solution corresponds to 1 per cent. of indigo blue. This method only gives accurate results if care be taken to expel the sulphurous acid formed by the impurities of the indigo.

Among the other substances contained in indigo there is a beautiful purple colouring matter, which, however, is only present in a very small quantity. This compound, which Schunck calls *indigo-rubin*, has the same composition as indigotin. It sublimes in beautiful purple crystals, and is more freely soluble in alcohol than indigotin. According to Schunck the young plants of *Polygonum tinctorium* do not contain any of it; it can only be obtained from plants which have attained an advanced stage of development, and in the cells of which the indican has already begun to undergo a molecular change. It may, however, be produced artificially by the action of alkalies on indican. Like indigotin it dissolves in alkaline liquids in presence of a reducing agent, forming a yellow solution, from which it is reprecipitated on exposure to the air. If it could be obtained in quantity it would be a most valuable purple colouring matter.

*Safflower* consists of the petals of *Carthamus tinctorius*, which is cultivated in many parts of Europe, Asia, Egypt, and South America. It contains *carthamin*, or *carthamic acid*, $C_{14}H_{16}O_7$, which is isolated by exhausting safflower with cold acidulated water to dissolve a yellow colouring matter. The residue, after washing, is treated with a dilute solution of soda crystals, and the liquid then precipitated by an acid. A red precipitate is obtained, which fixes itself on cotton thread immersed in the liquid, carthamin having the property of dyeing cotton without the intervention of a mordant, while the yellow colouring matter of safflower is not taken up at all by it. By treating the cotton again with soda-solution the carthamin is dissolved, and on addition of dilute sulphuric or tartaric acid obtained as a red precipitate, drying up to a beetle-green mass. Safflower dyes most delicate rose and pink shades, but unfortunately these colours are very fugitive, and do not stand exposure to the light.

*Archil* or *Orseille*.—Several lichens (species of *Rocella* and *Lecanora* principally) growing in different parts of the world contain a colourless crystalline compound called *orcin*, $C_7H_8O_2$, or various substances which yield orcin by the action of alkalies. In the presence of ammonia and air, orcin is changed into a true colouring matter called orcein. To this compound the formula $C_7H_7NO_3$ is generally assigned, but by recent researches Liebermann has shown that this body is a mixture of at least two compounds, having the compositiou $C_{14}H_{13}NO_4$ and $C_{14}H_{12}N_2O_3$.

To obtain the colouring matter the plants are exposed simultaneously to the action of air, ammonia, and moisture, at a moderate temperature, until they have acquired a deep purple colour. Thus a pasty and woody mass is obtained, commercially called *cudbear*. By treating the colouring matter with ammonia, and evaporating the solution to a suitable consistence, impure orcein, known as *archil* or *orseille*, is produced. It dyes on silk and wool a beautiful purple tint; but it is not a fast colour, and is now greatly superseded by the aniline colours.

*French purple* is a more stable colour. It is produced by exhausting the lichens with cold ammonia, precipitating the solution with hydrochloric acid, and dissolving the washed precipitate again in ammonia. On leaving this solution to stand in the air it soon assumes a cherry-red colour. It is now boiled for some time and then exposed in flat vessels to the air until it assumes a deep purple colour. On adding calcium chloride the purple compound is precipitated, while a red colour remains in solution. The calcium-lake is then decomposed with oxalic acid and the solution evaporated.

*Litmus*.—This colouring matter is derived from the same lichens which are used in the manufacture of archil. The dried and ground plants are mixed with ammonia and potassium carbonate, and the mixture is left standing until it assumes a violet colour. Then quicklime and urine are added, and the mass allowed to macerate for several weeks. It soon assumes a blue colour, and is then thickened with chalk or plaster of Paris and dried. Litmus is not used in dyeing or printing; its blue colouring matter is the potassium salt of a red acid, which has been obtained in the pure state by exposing an ammoniacal solution of orcin to the air, then adding soda-crystals, and heating the liquid to 60° to 80° C. in contact with the air, until it has changed into blue. On the addition of an acid red flakes are precipitated which do not dissolve freely in water, but readily in an alkali, with a blue colour.

As the value of the different "archil weeds" depends on the quantity of orcin contained in them, it is of the greatest importance for the manufacturer of these colours to have a method to determine quickly the percentage of orcin in a sample of these lichens. The old method for doing this is very inexact; it depends on the fact that a solution of orcin is coloured purple by bleaching powder, and the more intensely the more orcin is present. The colour thus produced is very unstable, and soon changes into orange-red and greenish yellow. Reymann has therefore lately proposed the following process for determining the percentage of orcin.

When an excess of bromine water is added to a diluted aqueous solution of orcin it is converted into insoluble tribromorcin, according to the following equation:—

$$C_7H_8O_2 + 6\,Br = C_7H_3Br_3O_2 + 3\,HBr.$$

If, therefore, bromine water of known strength be added to a solution of orcin until no more precipitate is formed, it is easy to calculate the quantity of orcin which is present. To be, however, certain that all the orcin is precipitated, an excess of bromine must be used; and this excess can also be readily determined by adding a standard solution of

potassium iodide, and determining the iodine which is set free by means of soda hyposulphite, just in the same way as it is done in the analysis of bleaching powder.

*Anotto* or *Annotta* is a preparation made from the pulp of the fruit of *Bixa orellana*, a tree growing in Central and Southern America. It contains a yellow compound called *orellin*, and an orange compound called *bixin*, $C_{15}H_{18}O_4$, which is insoluble in water, but readily dissolves in alcohol and alkalies with a deep yellow colour.

*Artificial Substantive Colours.*—The number of substantive colours which are prepared artificially is much larger than those occurring in nature. They are generally known by the name of *coal-tar colours*, and are all of a very recent origin. Not many years ago coal tar was an almost valueless bye-product in the manufacture of gas, and only of interest to the scientific chemist, who isolated from it a large number of various compounds. This black and fetid substance is, however, to-day employed in huge quantities for the manufacture of colours, which surpass in purity and richness of tint most of the dyes prepared from plants.

The following table gives a complete list of the compounds which so far have been isolated from coal tar:—

I. Hydrocarbons.

| | | Boiling point. |
|---|---|---|
| Butane or Butyl hydride, | $C_4H_{10}$ | 1° |
| Pentane or Pentyl hydride, | $C_5H_{12}$ | 38 |
| Hexane or Hexyl hydride, | $C_6H_{14}$ | 69 |
| Heptane or Heptyle hydride, | $C_7H_{16}$ | 99 |
| Octane or Octyl hydride, | $C_8H_{18}$ | 124 |
| Nonane or Nonyl hydride, | $C_9H_{20}$ | 148 |
| Decane or Decyl hydride, | $C_{10}H_{22}$ | 158 |
| Butylene, | $C_4H_8$ | 1° |
| Pentylene, | $C_5H_{10}$ | 39 |
| Hexylene, | $C_6H_{12}$ | 70 |
| Heptylene, | $C_7H_{14}$ | 100 |
| Octylene, | $C_8H_{16}$ | 125 |
| Nonylene, | $C_9H_{18}$ | 149 |
| Decylene, | $C_{10}H_{20}$ | 152 |

Solid Paraffin.

| | | Boiling point. |
|---|---|---|
| Benzol or Benzene, | $C_6H_6$ | 81° |
| Toluol or Toluene, | $C_7H_8$ | 111 |
| Isoxylene, | $C_8H_{10}$ | 138 |
| Paraxylene, | $C_8H_{10}$ | 136 |
| Pseudocumene, | $C_9H_{12}$ | 166 |
| Mesitylene, | $C_9H_{12}$ | 163 |
| Styrolene, | $C_8H_8$ | 146 |
| Hydronaphthalene, | $C_{10}H_{10}$ | 210 |

| | | | Melting point. |
|---|---|---|---|
| Naphthalene, | $C_{10}H_8$ | 217° | 80° |
| Diphenyl, | $C_{12}H_{10}$ | 240 | 70·5 |
| Acenaphthene, | $C_{12}H_{10}$ | 268 | 95 |
| Phenanthrene, | $C_{14}H_{10}$ | 340 | 100 |
| Anthracene, | $C_{14}H_{10}$ | — | 213 |
| Pyrene, | $C_{16}H_{18}$ | — | 142 |
| Chrysene, | $C_{18}H_{12}$ | — | 250 |

II. Phenols.

| | | Boiling point. | Melting point. |
|---|---|---|---|
| Phenol or Carbolic Acid, | $C_6H_6O$ | 181°·5 | 42° |
| Paracresol, | $C_7H_8O$ | 200 | 35·5 |
| Orthocresol, | $C_7H_8O$ | 190 | — |
| Phlorol, | $C_8H_{10}O$ | — | — |

III. Bases.

| | | | |
|---|---|---|---|
| Pyrrol, | $C_4H_5N$ | 133° | |
| Aniline, | $C_6H_7N$ | 181 | |
| Pyridine, | $C_5H_5N$ | 117 | |
| Picoline, | $C_6H_7N$ | 134 | |
| Lutidine, | $C_7H_9N$ | 154 | |
| Collidine, | $C_8H_{11}N$ | 176 | |
| Leucoline, | $C_9H_7N$ | 238 | |
| Iridoline, | $C_{10}H_9N$ | — | |
| Cryptidine, | $C_{11}H_{11}N$ | — | |
| Acridine, | $C_{12}H_9N$ | — | 107° |
| Carbazol, | $C_{12}H_9N$ | 351 | 238 |

Of this large list of compounds only a few are used for the manufacture of colours, which are conveniently divided into two groups:

(1) Colours derived from bases, or Aniline colours.

(2) Phenol colours.

*Colours derived from Bases, or Aniline Colours.*—In the year 1826 Unverdorben, a German chemist, discovered among the products of the destructive distillation of indigo an oily basic compound, which readily combines with acids, forming salts, which crystallize very readily and well, and therefore he called this compound *crystalline*. A few years afterwards another distinguished German chemist, Professor Runge, who was a great authority in the chemistry of colouring matters, found in coal tar a body which readily forms with acids crystalline salts, and possesses the property of imparting to a solution of bleaching powder a beautiful purple colour. He therefore designated it by the name of *cyanol*, or blue oil.

Somewhat later Fritzsche investigated the products which are produced by distilling indigo with potash, and observed among them a large quantity of a basic oily compound, which he analyzed and called *aniline*, from "anil," the Arabic name of indigo, and which means "the blue." About the same time Zinin found that benzene (or benzol, a hydrocarbon which was discovered by Faraday and which Mitscherlich obtained from benzoic acid), could be converted by certain reactions (see Aniline, page 205), into a basic compound, to which he gave the name of *benzidame*.

Subsequently A. W. Hofmann found, while working in Professor Liebig's laboratory, that *crystalline*, *cyanol*, *aniline*, and *benzidame* were identically the same substance, which henceforth was known by the name of aniline. Fritzsche had already observed that this body produced, with a solution of chromic acid, a blackish-blue precipitate; and Beissenhirtz, in 1853, found that when aniline is mixed with sulphuric acid and potassium dichromate a deep blue colour is produced.

These different observations were turned into practical account in 1856 by W. H. Perkin, who was the first to elicit the industrial value of aniline, which hitherto possessed only an interest for the scientific chemist. The so-called aniline colours are, however, not prepared from aniline alone, since in most cases two other bases, toluidine and pseudotoluidine, which are nearly related to aniline, are required for their preparation.

Aniline exists in coal tar only in a very small quantity, but, fortunately, it can be obtained indirectly from tar in any desired quantity; and it is now manufactured on a very large scale from

benzene or benzol, $C_6H_6$, which, as HOFMANN was the first to show, exists in light coal-tar oils.

*Aniline Purple or Mauve.*—This is the colour discovered by PERKINS, who obtained it by mixing cold dilute solutions of aniline sulphate and potassium dichromate. A black precipitate is formed on standing, containing only a few per cent. of mauve, which may be extracted by alcohol.

Although mauve is the most stable of the aniline colours, it is very expensive, and is now almost completely superseded by other aniline violets, which are much brighter and cheaper, though they are also much more fugitive.

*Rosaniline or aniline-red* is also known by the names of *fuchsine*, *magenta*, *solferino*, *azaline*, and *roscine*. Professor HOFMANN observed in 1843, while studying the action of fuming nitric acid on aniline, that a deep red colour was produced; but it was only in 1858 that the formation of a *crimson colouring* principle, and some of its characteristic properties, were first definitely pointed out by him. He, in studying the action of carbon tetrachloride on aniline, observed and described the formation of a basic substance, which dissolved in alcohol with a magnificent rich crimson colour.

The industrial discovery of aniline-red was made in 1859 by VERGUIN and RENARD BROTHERS of Lyons, who obtained it by the action of tin tetrachloride on aniline, and were the first to point out the importance of aniline-red for dyeing and printing, and to show that, by means of this colour, it was possible to obtain tints of a richness and purity superior to all that had been previously produced. They gave to their new colour the name of *fuchsine*, because it resembles that of the flower of the fuchsia.

Soon chemists found out that the formation of this colour was due to an oxidation of aniline, and many other processes were soon patented, the oxidizing agents being mercuric chloride or nitrate, lead nitrate, ferric sulphate, &c.

All these different agents were, however, soon superseded by the use of arsenic acid, which was patented by Dr. MEDLOCK in 1860.

The commercial product contains generally more or less of some violet colours; that which is quite free from it is called *roscine*.

The residues obtained in the manufacture of rosaniline are used for producing cheap red, purple, or brown colours, known as *cerise*, *ruby*, *grenade*, &c. They are simply mixtures of the yellow and purple colouring matters, with more or less rosaniline.

It may be stated here that magenta, as well as other aniline colours, are frequently adulterated with sugar. This falsification is easily effected by steeping finely crystallized sugar in an alcoholic solution of magenta, and allowing the alcohol to evaporate. As easily as this is done, so readily is it detected. It is only necessary to wash the suspected crystals with very strong alcohol, which dissolves the colour, and leaves the white sugar crystals behind. When such a mixture is kept in closed vessels for some time it becomes colourless, sugar, being a reducing agent, reduces the rosaniline to *leucaniline*, $C_{20}H_{21}N_3$, a colourless body, which contains 2 atoms of hydrogen more than rosaniline, and is readily produced by treating a solution of rosaniline with zinc and a dilute acid.

Magenta is now largely used by the Chinese and Japanese. A manufacturer, some years ago, thought he could increase his profits by sending them the colour adulterated with sugar; but not being aware of the reducing action of sugar, he packed the colour in well-closed tin cases, and was highly surprised when he heard that his goods, when arrived in Hong Kong, consisted of colourless crystals.

Rosaniline forms the starting point of a host of other most beautiful colours. By heating it with the iodides of methyl or ethyl, 1, 2, or 3 atoms of hydrogen are successively replaced by methyl or ethyl, and violet and purple colours are produced, which are known as HOFMANN'S violets. They are distinguished in commerce by the terms R, B, and B B. R is a red violet, consisting chiefly of the hydrochlorides of *methyl-rosaniline*, $C_{20}H_{18}(CH_3)N_3,ClH$, and *dimethyl-rosaniline*, $C_{20}H_{17}(CH_3)_2ClH$; while the bluish violet B contains the hydrochloride of the latter base, and that of *trimethyl-rosaniline*, $C_{20}H_{16}(CH_4)_3ClH$; and B B, which dyes a very blue shade, consists only of the last compound. The so-called *Paris violets* have a similar constitution; they are obtained by the action of oxidizing agents on a mixture of *methyl-aniline*, $C_6H_5NH(CH_3)$, and *dimethyl-aniline*, $C_6H_5N(CH_3)_2$, which are manufactured on a large scale by heating aniline-hydrochloride and methyl-alcohol under a very high pressure.

*Aniline Greens.*—These beautiful colours belong also to this group. That called *iodine-green* has the composition $C_{20}H_{16}(CH_3)_3N_3(C_6H_2(NO_2)_3O_2$, and occurs generally as a paste, which is sparingly soluble in water. The soluble-green, or methyl green, consists of $C_{20}H_{16}(CH_3)_5N_3I_2 + H_2O + ZnCl_2$, and crystallizes in splendid yellowish-green crystals having a copper-red lustre.

Before the discovery of iodine-green, another aniline-green was and is still used. It is prepared by adding aldehyde to an acid solution of rosaniline, and pouring the blue liquid thus obtained into a boiling solution of sodium thiosulphate (hyposulphite of soda). The *aldehyde-green* thus produced has the composition $C_{22}H_{27}N_3S_2O$.

The history of the discovery of this green is very curious. CHERPIN, a workman in the colour works of M. USÉBE, in Saint Ouen, near Paris, made experiments to fix the very unstable aldehyde-blue on tissues, without, however, succeeding. A friend of his, a photographer, to whom he mentioned it, said to him, "What, you cannot fix a colour; I will tell you how to do it. There is one substance which we use, and which fixes every thing, and that is hyposulphite of soda." CHERPIN took the advice, and to his great astonishment obtained a magnificent green.

Some dyers consider the aldehyde-green to be superior to the other aniline greens. As it is but seldom met with in commerce, we give in the following a practical method for its preparation.

Dissolve 1 lb. of magenta crystals in a mixture of 2 lbs. of concentrated sulphuric acid, and half a pound of water. This mixture is heated in a stoneware or glass vessel in a water bath to 75° C. Then 2 lbs. of good commercial aldehyde are added, and the liquid kept warm until it has assumed a pure blue colour. It is now slowly poured into a boiling solution of 4 lbs. of hyposulphite of soda in 10 gallons of water. When cold, the liquid is filtered, and is now ready for dyeing.

*Phenylrosaniline.*—When rosaniline is heated with aniline in the presence of benzoic acid, or other organic acids, ammonia is given off, and hydrogen is replaced by the group *phenyl*, $C_6H_5$.

The salts of *monophenyl rosaniline*, $C_{20}H_{18}(C_6H_5)_2N_3$, dye a reddish-violet, and those of *diphenyl rosaniline*, $C_{20}H_{17}(C_6H_5)N_3$, a bluish violet. The so-called *night blue* consists of a perfectly pure salt of *triphenyl rosaniline*, $C_{20}H_{16}(C_6H_5)_3N_3$: while mixtures of this with the preceding compounds are known by the terms B, B B, B B B and B B B B, the first having the most, and the last the least reddish shade. These compounds are sparingly soluble in water, but freely in alcohol.

*Soluble Blues.*—When triphenyl rosaniline is dissolved in sulphuric acid, and water is added, a dark blue mass, drying up to grains having a golden lustre, is precipitated. This consists of *triphenyl rosaniline sulphonic acid*, $C_{20}H_{16}(C_6H_5)_2(C_6H_4SO_3H)$, and stands consequently in the same relation to triphenyl rosaniline as sulphopurpuric acid to indigo. Its sodium salt, which forms a grey amorphous mass, dissolving with a beautiful blue colour in water, is found in commerce under the name of *Nicholson's blue*. By the further action of sulphuric acid, other sulpho-acids are formed, occurring as sodium salts in several *soluble aniline blues* or *alkali blues*.

*Benzyl-rosaniline.*—When a mixture of methyl alcohol, methyl iodide, rosaniline, and benzyl chloride, $C_8H_7Cl$, which is obtained by the action of chlorine on boiling toluene, is heated to 100° C., the compound $C_{20}H_{16}(C_6H_5CH_2)N_3CH_3I$ is formed, crystallizing in beetle green needles. The salts of this ammonium base dye on silk a rich reddish violet.

*Chrysaniline* or *Phosphine*, $C_{20}H_{17}N_3$, is a bye-product in the manufacture of rosaniline. It forms yellow crystalline salts, dyeing on silk a deep yellow shade.

*Saffranine*, $C_{21}H_{20}N_4$.—This body is a derivative of pseudotoluidine, and obtained by treating high-boiling commercial aniline first with nitrous acid, and then with arsenic acid, or other oxidizing agents. The hydrochloride, $C_{21}H_{20}N_4.ClH$, occurs in commerce in the form of a paste or reddish powder; it is very soluble in water, but not in a solution of salt, and dyes on silk most delicate rose-tints. It is therefore largely used as a substitute of safflower. It dissolves in concentrated sulphuric acid with a splendid green colour. On gradually adding water to this solution, the colour changes successively into greenish-blue, blue, purple, violet, and finally into red.

*Diphenylamine Blue.*—This colour is produced by heating commercial diphenylamine (a mixture of diphenylamine and ditolylamine) with sesquichloride of carbon gradually to 180°.

When methylaniline is heated with aniline hydrochloride under strong pressure, it is converted into *methylphenylaniline*, $(NC_6H_5)_2CH_3$, a liquid which, when heated with sesquichloride of carbon, yields a magnificent purple colouring matter.

*Phenylene Brown.*—This compound, which is also called *Manchester brown* and *Bismarck brown*, is the hydrochloride of triamidoazobenzene, $C_{12}H_{13}N_5$. It is obtained by heating benzene with a mixture of nitric and sulphuric acids, which convert it into solid, crystalline *dinitrobenzene*, $C_6H_4(NO_2)_2$. By acting on this body with tin or zinc and hydrochloric acid it is reduced to *diamidobenzene* or *phenylenediamine*, $C_6H_4(NH_2)_2$, which is dissolved in hydrochloric acid, and then acted upon by sodium nitrite.

$$2C_6H_8N_2 + NO_2H = C_{12}H_{13}N_5 + 2H_2O.$$

Phenylene brown is chiefly used for dying a rich brown on wool and silk.

*Magdala red*, *Naphthalene red*, is the hydrochloride of the base, $C_{30}H_{21}N_3$, and is obtained from naphthalene, $C_{10}H_8$, a hydrocarbon which exists in a large quantity in coal tar. Nitric acid converts it into *nitronaphthalene*, $C_{10}H_7NO_2$, which is easily transformed into *amido-naphthalene* or *naphthylamine*, $C_{10}H_7NH_2$, by the same reactions by which aniline is obtained from nitrobenzene. It forms crystalline salts, yielding with oxidizing agents a blue precipitate, which soon changes into a purple powder of *oxynaphthylamine*, $C_{10}H_7ONH_2$. On adding sodium nitrite to a solution of naphthylamine hydrochloride a crystalline precipitate of *amidoazonaphthalene*, $C_{20}H_{15}N_3$, is formed. This compound crystallizes in yellow needles, and dyes on silk a fine orange, and forms salts with acids, having an intensely purple colour, but they are very unstable. Thus, on dipping silk which is dyed with the base in hydrochloric acid it turns purple, but on washing with water becomes again orange. When amidoazonaphthalene is heated with naphthylamine Magdala red is produced. It dissolves in alcohol and water with a red colour, and the dilute alcoholic solution exhibits a splendid garnet-red fluorescence. It dyes on silk and wool a delicate red, showing the same fluorescence as the alcoholic solution.

Phenol Colours.—*Phenol* or *Carbolic Acid*, $C_6H_6O$, occurs in large quantities in coal tar, and is the type of a group of compounds which, like aniline and its homologous bases, are nearly allied to the different hydrocarbons existing in tar. The following coloured derivatives of phenols are used in dyeing:—

*Picric Acid* or *Trinitrophenol*, $C_6H_3(NO_2)_3O$, is readily formed by the continued action of nitric acid on phenol and many other bodies, such as indigo, aloes, gum resins, silk, wool, &c. It was formerly prepared from acaroid resin, but is now obtained by dissolving phenol in sulphuric acid, and treating this solution with sodium nitrate or nitric acid. Picric acid crystallizes from hot water in

pale-yellow plates, having an intensely bitter taste, and forms salts, which have a yellow or orange colour and are very explosive. When picric acid is dissolved in a warm solution of potassium cyanide an intensely red liquid is obtained, containing the potassium salt of *isopurpuric acid*:

$$C_6H_3N_3O_7 + 3CNK + 2H_2O = C_8H_4N_5O_6K + CO_3K_2 + NH_3.$$

This salt crystallizes in small reddish-brown plates, having a beetle-green lustre. The corresponding free acid is not known, but a number of its salts have been obtained. Thus, on acting on the potassium salt with ammonium chloride, we obtain *ammonium purpurate*, $C_8H_4N_5O_6(NH_4)$, which dissolves in water with beautiful red colour, and is used for dyeing wool and silk. When chloride of barium is added to a solution of one of these salts a vermilion red precipitate of barium isopurpurate is formed.

A compound nearly allied to phenol is cresol, $C_7H_8O$, which also is found in tar, and yields yellow compounds when treated with nitric acid.

*Victoria-yellow* or *aniline-orange* consists principally of the sodium salt of a *dinitrocresol*, $C_7H_6(NO_2)_2O_2$. Its preparation is not known. A similar colouring matter consists of the potassium salt of another *dinitrocresol*. It forms red crystals, and was exhibited in Vienna under the name of *gold-yellow*.

*Manchester-yellow* or *Naphthalene-yellow* consists of the sodium or calcium salts of *dinitronaphthol*, $C_{10}H_6(NO_2)_2O$. This compound, which crystallizes in lemon-yellow needles, and forms salts having a deep-yellow or orange colour, is manufactured by treating a solution of naphthylamine hydrochloride with sodium nitrite, and boiling the product with nitric acid. It crystallizes in lemon-yellow needles. The commercial product consists of the sodium or calcium salt of this body, which is also now manufactured by the following process:—

Equal parts of naphthalene and concentrated sulphuric acid are heated to 100°. Thus *naphthalene sulphonic acid*, $C_{10}H_7SO_3H$, is produced, which by fusing with an alkali is transformed into naphthol, $C_{10}H_8O$:

$$C_{10}H_8SO_3 + 2NaOH = C_{10}H_8O + K_2SO_3 + H_2O.$$

Naphthol is a body resembling phenol, and is converted into naphthalene-yellow by dissolving it in sulphuric acid and adding nitric acid to this solution.

$$C_{10}H_8O + 2NO_3H = C_{10}H_6(NO_2)O + 2H_2O.$$

Naphthalene-yellow is a very rich and pure colour, dyeing on silk and wool all shades between lemon-yellow and golden-yellow, without showing that greenish reflection which the yellow produced by picric acid exhibits. Its tinctorial power is also very great, one part being quite sufficient to dye on 200 parts of wool a deep yellow.

*Aurin or Yellow Corallin*, $C_{20}H_{14}O_3$.—This compound, which is also called *rosolic acid*, and used for dyeing on silk and wool a fine orange, is obtained by heating phenol with sulphuric acid and oxalic acid.

$$3C_6H_6O + 2CO = C_{20}H_{14}O_3 + 2H_2O.$$

The commercial product is a brittle mass, having a beetle-green lustre. In the impure state it appears quite amorphous; but lately a purer product has been brought into the market by Messrs. Roberts, Dale, & Co., which is distinctly crystalline. The chemically pure compound is a beautiful substance, forming prisms or needles, having either the colour of chromic acid and a brilliant diamond lustre, or of a darker shade with a blue or greenish-blue reflection. In alkalies it dissolves with a magenta-red colour.

*Peonin* or *Red Corallin* is obtained by heating aurin with alcoholic ammonia under pressure. It differs from aurin by dyeing a bright red shade. The pure compound crystallizes in small bronze-coloured needles. Its composition is not known.

*Azulin* or *Azurin* is a blue colouring matter, which is formed by heating aurin with aniline. Its composition is not known, and it is now quite superseded by the aniline-blues.

*Eosin* is a colouring matter having very great resemblance to Magdala-red, but its constitution is quite different. The commercial product is a brown crystalline powder, dissolving in water with a red colour, and exhibiting a splendid greenish fluorescence. It dyes on silk a most delicate pink, showing a rich scarlet fluorescence. Its composition is $C_{20}H_6Br_4O_5K_2$, being the potassium salt of *tetrabromofluorescein*.

Fluorescein was discovered by Professor Baeyer. It is obtained from resorcin, $C_6H_6O_2$, a body which is very nearly allied to common phenol, as well as to orcin, $C_7H_8O_2$ (see *Archil*). On heating this compound with *phthalic acid*, $C_8H_6O_4$ (a product of the oxidation of naphthalene), fluorescein is formed according to the equation—

$$2C_6H_6O_2 + C_8H_6O_4 = C_{20}H_{12}O_5 + 3H_2O.$$

Fluorescein forms small brown crystals, dissolving in ammonia with a red colour. This solution exhibits, even if very dilute, a splendid green fluorescence. By acting with bromine on it the tetra-bromo compound is formed, yielding with alkalies red salts. The name eosin is derived from Ἠώς, "aurora." When an aqueous solution of eosin is heated with sodium amalgam it becomes colourless; on adding now one or two drops of a solution of potassium permanganate the liquid becomes deep-green and apparently opaque, but on pouring it into a large quantity of water a solution is obtained having a reddish colour and exhibiting a most beautiful green fluorescence, being due to the formation of fluorescein.

*Aloës-purple.*—When aloës is heated with nitric acid it is first converted into *aloëtic acid*, $C_{14}H_4(NO_2)_4O_2$, which, by the further action of the acid, is oxidized to *chrysammic acid*, $C_{14}H_2(NO_2)_4O_4$.

*Aloëtic acid* is a crystalline orange-yellow powder, forming red coloured salts, which are explosive.

*Chrysammic Acid* crystallizes in small brilliant, golden-yellow plates, dissolving in alcohol or boiling water with a beautiful red colour. Its crystalline salts are very slightly soluble in water and very explosive. They have a red colour, and exhibit a beautiful bronze or beetle-green lustre.

An impure mixture of these two acids is used for dyeing red and brownish-red colours on silk and wool. It has also been applied to cotton as a steam-colour, producing a violet. Mixed with garancin or artificial alizarin, it produces on mordanted cotton garnet-red shades, having a peculiar lustre.

The two acids obtained from aloës are nearly related to the colours contained in madder, and belong to the group of phenol colours.

*Murexide*, $C_8H_5N_5O_7,NH_3$.—This colouring matter must be mentioned, because it was largely used before the discovery of the aniline colours as a brilliant red dye-stuff. It was discovered in 1835 by LIEBIG and WÖHLER, but has been only manufactured and employed in dyeing and printing since 1857. It is obtained from uric acid, a compound existing in the urine of all animals, and found in large quantities in guano, from which it is extracted by treating it with hydrochloric acid, exhausting the residue with hot potash, and adding to the solution thus obtained dilute sulphuric acid, by which the uric acid is precipitated as a white insoluble powder. To convert it into murexide it is dissolved in cold nitric acid, the solution carefully evaporated to dryness, and the residue treated with ammonia, in which it dissolves with a splendid purplish-red colour. The pure compound crystallizes in small red prisms, having a beetle-green lustre, and dissolves readily in water. On silk and wool it dyes a beautiful red colour.

ADJECTIVE COLOURS.—Almost all the colouring matters belonging to this group occur in various plants and animals. Only a very few have been prepared artificially.

*Madder* is the root of *Rubia tinctorum*, a plant growing in the south of Europe and the Levant. It is largely cultivated in Holland, France, Italy, Southern Prussia, and Turkey. The plant is very nearly allied to the sweet wood-ruff (*Asperula odorata*). It is about three feet high, and has a fibrous root, which is the part used in dyeing. The best roots vary in size between a writing quill and a small finger. They are in the fresh state semi-transparent, of a reddish colour, and possess a peculiar smell. They are collected after two or three years' growth, and dried either in the open air or in stoves. The filaments, and the epidermis (called *mull*), and the pith are removed, leaving nothing but the ligneous fibre. The madder, after being thus purified, is ground in a mill with vertical stones, and then passed through sieves of different fineness. The product thus obtained is distinguished according to its origin into Dutch, Alsatian, Avignon, Naples, Russia, and Turkey madder. Madder is undoubtedly one of the most valuable and interesting dyeing materials, and has been subjected to more chemical researches than any other colouring matter. The discussion on this subject seems to be settled now, it being generally acknowledged that the views of ROBIQUET and SCHUNCK are correct, according to which the finest and most permanent dyes are yielded by *alizarin*, $C_{14}H_8O_4$, while *purpurin*, $C_{14}H_8O_5$, and other coloured compounds contained in the root yield tints of but little stability.

*Alizarin*, $C_{14}H_8O_4$.—This compound, which has obtained its name from *alizari*, the oriental name of madder, does not exist in the free state in fresh madder, but as a glucoside, called by SCHUNCK *rubianic acid* and by ROCHLEDER *ruberythric acid*, $C_{26}H_{28}O_{14}$. This body, which also occurs in *Morinda citrifolia*, is obtained by exhausting the fresh root with water, and adding to the solution lead acetate, in order to precipitate several organic acids and other bodies. The filtrate yields with basic lead acetate a precipitate of lead rubianate, which is decomposed by sulphuretted hydrogen. On evaporating the solution rubianic acid crystallizes in yellow, glistening, silky needles. It is decomposed by boiling it with dilute acids or alkalies into alizarin and grape sugar, according to the following equation.—

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6.$$

The same decomposition is produced by the action of a ferment which exists in the root, and has been called by SCHUNCK *erythrozyme*. For this reason madder is only used in dyeing after having been kept for some years, during which an internal fermentation goes on.

Alizarin crystallizes from spirits of wine in yellowish-red needles, containing three molecules of water, which escape at 100° C. On heating it carefully to a higher temperature it sublimes in brilliant red needles, which dissolve but sparingly in water, but freely in alcohol and ether. In ammonia it dissolves with a purple colour, and with potash and soda it yields a solution which in transmitted light appears of a deep bluish purple, and in reflected light of a pure blue. When a solution of the chlorides of barium or calcium is added to an ammoniacal solution of alizarin, or to a solution which has been prepared by boiling an excess of alizarin with a caustic lye, blue precipitates are obtained, having the composition $C_{14}H_6O_4Ba$, or $C_{14}H_6O_4Ca$. Aluminium acetate (red liquor) produces in the alkaline solution a red precipitate, and ferrous acetate or other iron salts give a dark blackish-violet precipitate. When copper acetate is added to an alcoholic solution of alizarin a characteristic purple precipitate is formed. The property of alizarin to form insoluble coloured metallic compounds is made use of in dyeing and printing, as we shall see farther on.

*Purpurin*, $C_{14}H_8O_5$, crystallizes from alcohol in yellow needles, and sublimes on heating in red needles, dissolving in alkalies with a dark red colour. These solutions yield purple precipitates, with calcium and barium salts.

Purpurin has been produced artificially by heating alizarin with sulphuric acid and manganese dioxide.

*Pseudo-purpurin*, $C_{14}H_{18}O_6$, is another colouring matter existing in madder root. It is a very unstable body, which is very easily transformed into purpurin.

Besides these compounds madder contains a number of orange and brown colouring matters, citric

acid, oxalic acid, pectic acid, fats, resins, gums, and other bodies.

Alizarin is now prepared artificially on a very large scale. Before, however, entering into this subject, it will be convenient to describe first some improvements in the treatment of madder, which have been successively introduced of late years, and which are all directed to the purification of madder. These processes have become more or less obsolete since the discovery of artificial alizarin.

The object of all the different processes is to free the alizarin and purpurin as much as possible from the other bodies found in the root, for the more of these that are removed the easier and the more rapid is the process of dyeing, and the purer and richer are the colours. The portion of the cloth which is to remain white is also less liable to be soiled, and thus the printed goods require less clearing, which always, to some extent, affects the colours.

*Garancin* was first prepared by LAGIER, ROBIQUET, and COLIN, by treating ground madder for some time with less than one-third of its weight of concentrated sulphuric acid; then water is added, and the mixture is boiled. The product is washed, dried, and ground with some chalk or sodium carbonate, to neutralize any free acid which may be retained by the fibre as well as the pectic acid, which has been set at liberty, and which can only be removed by continued washing with water.

*Pincoffin*, which was first brought into the market by Messrs. PINCOFFS & Co., Manchester, is a kind of garancin, which is prepared and washed with very great care, and heated with high-pressure steam. Pincoffin yields very bright colours, and especially very pure lilacs.

*Flower of Madder* (*Fleur de Garance*) is obtained by steeping finely-ground madder-root in acidulated water, and then washing with water and pressing and drying the residue. The product is free from calcium carbonate, gum, sugar, and the yellow and brown colouring matters.

*Madder Extracts.*—The preparations which have just been described contain more or less of the woody fibre, which, of course, increases the expense of carriage. Therefore, attempts have been made to get rid of these impurities, and to prepare an extract of the root, consisting chiefly of more or less pure alizarin and purpurin. The manufacture of the extracts has been carried on on a large scale, but during the last few years they have been almost completely superseded by artificial alizarin. It will, therefore, only be necessary to give the outlines of the more important processes for obtaining these extracts, which are not obtained directly from madder, but from garancin and other similar preparations.

*Alkali Process.*—Madder, or one of its preparations, is exhausted with dilute ammonia or soda, the solution precipitated with sulphuric acid, and the precipitate, after washing, is boiled with dilute sulphuric acid.

*Spirit-extract* is obtained by exhausting flowers of madder or garancin with wood-spirit or common spirit, and distilling the spirit from the solution.

*Extraction of Alizarin from Madder.*—Fresh madder root, in which the rubianic acid is not yet altered, is ground and treated with an aqueous solution of sulphurous acid, which prevents fermentation of the rubianic acid. The liquid is then filtered, the residue pressed, and the solution mixed with 3 per cent. of sulphuric acid of 1·52 spec. grav. On heating to 30° to 40° C. purpurin separates in red flakes, which are separated by filtration. The filtrate yields on boiling a precipitate of alizarin, which, owing to the presence of an impurity, has a greenish-black colour.

*Preparation of Artificial Alizarin.*—GRAEBE and LIEBERMANN discovered in the year 1868 that alizarin stands in a very close relation to *anthracene*, $C_{14}H_{10}$, a solid hydrocarbon contained in coal tar. They succeeded not only in reducing alizarin to anthracene, but also in converting the latter into the colouring matter. ANDERSON had already found that when anthracene is heated with nitric acid it is oxidized to a yellow crystalline body, which he called *oxyanthracene*, $C_{14}H_8O_2$, and which is now known as *anthraquinone*. On heating this body with bromine it yields *dibromanthraquinone*, $C_{14}H_6Br_2O_2$, and on melting this with caustic potash, it is converted into alizarin according to the following equation—

$$C_{14}H_6Br_2O_2 + 2KOH = C_{14}H_8O_4 + 2KBr.$$

This discovery would, however, have been but of little practical value, if GRAEBE and LIEBERMANN had not succeeded in replacing the bromine by cheaper materials. (See page 513.)

Artificial alizarin occurs in commerce in the form of yellow or brown paste, containing besides alizarin and water several other products. Of these, however, only one is of practical value. It was discovered by PERKIN, who calls it *anthrapurpurin*, $C_{14}H_8O_5$, having the same composition as purpurin, but quite different properties. In the pure state it forms minute orange needles, and yielding with the alkalies, &c., reactions very similar to those of alizarin. It has about the same affinity for mordants as alizarin, giving similar shades, but the reds are much brighter and purer, the purples more blue, and the blacks more intense. When artificial alizarin first appeared in the market, printers found it very difficult to produce always the same shades, which was owing to the fact that it contained alizarin and anthrapurpurin in varying proportions. This difficulty has now been removed, by separating the colouring matters as much as possible; that consisting of almost pure alizarin, which dyes a bluish-red, being called "blue alizarin," while anthrapurpurin goes by the name of "red alizarin." GRAEBE and LIEBERMANN'S discovery forms an epoch in the history of organic chemistry, alizarin being the first natural dye-stuff which has been prepared artificially. Since that time the manufacture of alizarin from anthracene has assumed large dimensions. According to the official report on the Vienna exhibition of 1873, there existed already in Germany ten to twelve such works, while England and France possessed, on account of the patent-laws, each only one alizarin works. The total quantity of

alizarin which was manufactured in 1873 was 22,000 cwts. of alizarin paste, containing 10 per cent. of colouring matter, and representing a value of £600,000; while the total amount of madder which hitherto has been used per annum may be estimated at 1,000,000 cwts., with a value of about £2,000,000. It can fairly be assumed that there exists in coal tar a quantity of anthracene which is more than sufficient to manufacture all the alizarin which is contained in the above quantity of madder. This fact is from a politic-economic point of view of the highest importance, for the growth of madder requires a rich soil and occupies several years. For the benefit of mankind this land would be much better employed for the growth of cereals.

*Munjeet* or *Indian madder* consists of the stems of *Rubia munjista*. It contains no alizarin, but purpurin and *munjistin*, both having probably the same composition. Munjistin crystallizes in yellow plates, dissolving in alkalies with a crimson colour. It dyes on an alum-mordant an orange, and on an iron-mordant a brownish purple.

*Brazil wood*, *Lima wood*, *Peach wood*, &c., are derived from different species of *Cæsalpinia* growing in South and Central America; while *Sapan wood* comes from India, Japan, and China. They contain a glucoside which is very little known, being easily resolved into a kind of sugar, and into *brasilin*, $C_{22}H_{20}O_7$, crystallizing from water or alcohol in large yellowish prisms, often found in quantity in the extract of the above woods when prepared on a large scale. Brasilin dissolves in alkalies with a crimson colour. This solution gives with aluminium salts and stannic salts a blackish violet precipitate. When nitric acid is added to a solution of brasilin a red crystalline body called *brasilein* $(C_{22}H_{19}O_7)_3N$, is formed. The same oxidation takes place slowly in the air in the presence of ammonia, and therefore an aqueous solution of brasilin, which when freshly prepared is almost colourless, assumes on standing a yellowish-red colour.

*Logwood* or *Campeachy wood* is the wood of *Hæmatoxylon campechianum*, a tree occurring in South and Central America. It contains *hæmatoxylin*, crystallizing from water in large yellow prisms, consisting of $C_{16}H_{14}O_6 + 3\,H_2O$, and having a sweet taste. When perfectly pure it forms with bases colourless salts, which, however, in the presence of air and ammonia colour red or purple. The coloured compound thus formed has been called *hæmatein* $(C_{16}H_{13}O_6)_3N$, and is also produced by adding fuming nitric acid to a solution of hæmatoxylin in ether. It forms brownish-red crystals, having a green lustre. Hæmatein exists also in the free state in the wood, and a decoction of it gives, therefore, the following reactions.

Alkalies change it first into red and then into violet.

Baryta and lime give blue precipitates, and ferric salts a bluish-black precipitate. Stannous chloride produces a violet precipitate; and an alkaline solution of alumina gives an abundant bluish-violet precipitate. This latter reaction is very characteristic, and serves to detect easily the presence of logwood in a mixture.

*Red Sanders Wood* or *Santal Wood* is obtained from *Pterocarpus santalinus*, a small tree growing in southern India. It contains *santalin*, $C_{15}H_{14}O_5$, forming microscopic red crystals, which are insoluble in water, but dissolve in alcohol with a red and in alkalies with a violet colour. Similar woods are *camwood* and *barwood*, which comes from *Baphia nitida*, a tree growing in Sierra Leone.

*Cochineal* consists of the dried bodies of a small insect, *Coccus cacti*, belonging to the family of the gall insects, living on a species of cactus in Mexico and Central America, but now also cultivated in the Canaries, Java, Algiers, and Spain. The colouring matter of cochineal is *carminic acid*, $C_{17}H_{18}O_{10}$, and is prepared by exhausting cochineal with boiling water, and precipitating the solution with lead acetate. The precipitate after being washed is decomposed with sulphuretted hydrogen, and the filtrate evaporated at a low temperature. Carminic acid is a brownish-purple powder, and forms red or purple salts. (See p. 535.)

The splendid pigment "carmine" is obtained by boiling cochineal with water and alum, and leaving the solution to stand. Carmine is gradually precipitated as a fine powder; its chemical nature is not understood; it generally contains alumina, which, however, is not essential to it, the colouring matter being completely soluble in ammonia.

Carminic acid or compounds of very similar properties exist also in the following drugs:—

*Kermes* consists of the bodies of *Coccus ilicis*, living in south Europe on the leaves of the prickly oak (*Quercus ilicis*).

*Lac-dye* is the product of *Coccus ficus*, living on the young branches of *Ficus religiosa* and other trees growing in eastern Asia. The insect produces by puncturing the bark an exudation, by which the twigs become incrustate with a brownish-red resin called *stick-lac*. On grinding this product and boiling it with water, *shellac* is left behind; and a solution is obtained, which leaves on evaporation lac-dye, which is found in commerce in the form of small square plates.

*Ammoniacal Cochineal.*—When carminic acid is treated for some time with ammonia, it is converted into a violet or purple colouring matter. Ammoniacal cochineal is prepared by macerating three parts of ammonia with one part of ground cochineal in a closed vessel during a month. To the clear liquid is then added 0·4 parts of gelatinous alumina, and the mixture evaporated to dryness at a gentle heat. A quicker and apparently a better method is to heat unground cochineal and ammonia together in a closed vessel for eight to ten hours at 100° C., and concentrating the solution by evaporation.

*Quercitron* is the bark of *Quercus tinctoria* or black oak, which is found abundantly in the southern parts of the United States. It contains *quercitrin*, $C_{33}H_{30}O_7$, which forms small yellow crystals which dissolve but sparingly in water, but readily in alkalies with a greenish yellow colour. When quercitrin is

boiled with dilute sulphuric acid it is split up into a kind of sugar, called *isodulcite*, $C_6H_{12}O_5$, and into *quercetin*, $C_{27}H_{28}O_{12}$, which also occurs in other plants. It forms a crystalline lemon-yellow powder, is almost insoluble in water, but dissolves in alkalies with a reddish yellow colour. Its alcoholic solution yields with several metallic salts orange precipitates. *Flavin* is a commercial product which is prepared from quercitron, and is chiefly a mixture of quercitron and quercetin. English flavin appears to consist of almost pure quercetin. There exist several other dye-stuffs which are nearly related to quercitron. Thus the *Chinese berries* or the fruit of *Sophora japonica* contain *melin;* the common garden-rue (*Ruta graveolens*), the leaves of the holly, capers, and buck wheat (*Polygonum fagopyrum*), contain *rutin*, while *robinin* is found in the common white acacia (*Robinia pseud-acacia*). These three compounds have great resemblance to quercitrin, and yield as products of decomposition peculiar kinds of sugar and quercetin.

*French* and *Persian Berries* are the fruit of *Rhamnus infectoria* and other species of rhamnus growing in different parts of Europe and Asia. They seem to contain different glucosides, yielding as products of decomposition *quercetin* and *rhamnetin*, $C_{12}H_{10}O_5$, which is a body resembling quercetin.

*Fustic* consists of the wood of *Morus tinctoria*, a tree growing in the West Indies and South America. It contains two distinct colouring matters.

*Moritannic acid*, or *Maclurin*, $C_{13}H_{10}O_6 + H_2O$, is readily soluble in hot water, and forms yellow crystals. It gives a greenish-black precipitate with ferrous sulphate, and a yellow one with lead acetate.

*Morin*, $C_{12}H_8O_5$, is only sparingly soluble in water, and crystallizes from alcohol in pale yellow needles, dissolving with a yellow colour in alkalies. This solution gives, with several metallic salts, yellow precipitates.

*Weld* is the plant *Reseda lutea*, which is cultivated in England, Germany, and France. It is dried entire, and contains a yellow colouring matter, *luteolin*, $C_{12}H_8O_5$, which crystallizes from hot water in fine yellow needles, dissolving with a dark yellow colour in alkalies.

*Fustet*, or *Young Fustic*, is the wood of *Rhus cotinus*. It contains a yellow colouring matter, but is not much used, because the colours which it dyes are very fugitive.

*Turmeric* is the root of *Curcuma longa*, a plant which is cultivated in Southern Asia. It contains *curcumin*, $C_{10}H_{10}O_3$, which is insoluble in cold water and sparingly in boiling water, but dissolves freely in alcohol, and forms brilliant yellow crystals. When turmeric paper is moistened with a solution of boric acid and then dried, it assumes an orange colour, which by alkalies is changed into blue. This is caused by the formation of a compound which is called *rosocyanin*. Its composition is unknown. It forms needles showing a beetle-green lustre, and dissolving in alcohol with a splendid red colour, which, on adding a drop of soda, changes into a deep blue. Lime and baryta water give blue precipitates with the alcoholic solution.

*Chica*, or *Caracuru*, is a red colouring matter, which, like annotto, is used by the Indians in South America for painting their bodies. It is obtained from the leaves of *Bignonia chica*, a large climbing shrub. On boiling the leaves with water, and adding to the decoction the bark of a tree called *Arayane*, a red colouring matter is precipitated. When dry it forms a red mass, which on rubbing assumes a beetle-green lustre. It dissolves in alkalies with an orange colour, and is used for dyeing orange and red shades.

*Purree*, or *Indian yellow*, is a substance of unknown origin, which is imported from India and China. It consists chiefly of the magnesium salt of *euxanthic acid*, $C_{19}H_{16}O_{10}$. The free acid forms yellow silky crystals, having a sweetish bitter taste.

*Chinese green*, or *Lo-kao*, occurs in commerce in small scales or plates, having a bluish colour with a green or violet reflection. It is prepared in China from *Rhamnus utilis* and *R. chlorophorus* by exhausting the bark of these shrubs with hot water, and immersing pieces of bleached, but not mordanted, cotton into the infusion. In the evening it is spread on grass, and during the night the upper side colours green. Early in the morning it is removed, dried, and repeatedly treated again as above, until the cloth is super-saturated with the colour. Then it is washed with cold water, and the wash water placed in a boiler and covered with a layer of cotton yarn, from which on boiling the liquid takes up the colour. This process is again repeated, using the same cotton, which when charged with sufficient colour is again washed with cold clear water, and at the same time well beaten or rubbed with the hands to detach the colouring matter, which is collected and dried on paper. From this process it would appear that Lo-kao is the product of oxidation of some colourless compound contained in the plants, and is probably a mixture of a blue and a yellow colouring matter.

*Croissant* and *Bretonière's New Colours*, which quite recently have appeared in the market, are obtained by fusing sawdust, bran, old paper, or other refuse, with sodium sulphide. They form a black porous mass, possessing a very disagreeable alliaceous odour, and dissolve in hot water with a more or less dark brown or greenish-black colour, and yield with different metallic salts precipitates of various shades. According to the Bulletin of the Industrial Society of Mulhouse, they may be employed for dyeing or printing grey, greyish-brown, yellowish-brown, and yellow shades, which are exceedingly stable and fast. Although such shades can be obtained by the old dyes, they are more expensive and less durable. Owing to the facility with which the new colours can be fixed, it may be expected that they will be used for certain simple goods, of which a great durability in colour is demanded.

*Tannic Acids.*—The following compounds, thus commonly termed, are a group of colourless bodies existing in several plants, which yield under the

influence of a peculiar process of oxidation, or of mordants, brown, grey, or black colouring matter. They are all soluble in water, have an acid reaction, and an astringent taste. They are precipitated from their solution by tartar emetic, salts of tin, and gelatin, and yield with ferric salts bluish-black or dark green precipitates.

*Catechu*, *Cutch*, or *Terra japonica*, is the extract of the wood of *Acacia catechu*, which grows in India and Burmah, and of *A. suma*, growing in Mysore and Bengal. It contains *catechin* or *catechuic acid*, $C_{13}H_{12}O_5$, in minute acicular crystals, which are sparingly soluble in water. Its aqueous solution gives with ferric chloride a green coloration. When catechin is boiled for some time with water in contact with the air it is converted into catechutannic acid, which also exists ready formed in catechu; it is freely soluble in water, and resembles tannin, from which it differs by yielding with ferric chloride a dark green precipitate. A product analogous to catechu is *Areca-nut catechu*, which is obtained from the seeds of *Areca catechu*, or *Betel nuts*. It does not seem that this body forms a part of the catechu of commerce.

*Gambier* or *Pale Catechu* is obtained from *Uncaria gambier*, a climbing shrub growing in the countries bordering the Straits of Malacca, and from *U. acida*, which is found in the Malayan islands. Gambier is obtained by boiling the leaves with water, and evaporating the decoction. It contains the same compounds which exist in common catechu.

*Kino* is the dried juice of *Pterocarpus marsupium*, a tree common in India; it contains *kinotannic acid*, which gives with ferric salts a green precipitate.

*Tannin* consists chiefly of *gallotannic* or *digallic acid*, $C_{12}H_{20}O_9$, existing in a great number of plants. It is obtained by exhausting nut-galls or Chinese galls either with commercial ether or better with absolute ether containing 5 per cent. of absolute alcohol, and distilling the ether off. It forms a pale yellow amorphous powder, having a very astringent taste. With ferric salts it gives a bluish black precipitate.

The following substances containing tannin are used in dyeing:—

*Nut-galls* are obtained from *Quercus Lusitanica*, a small kind of oak found in Greece, Asia Minor, and Syria. The tender shoots of this shrub are pierced by the female of a small insect (*Cynips gallae tinctoriae*) which deposits one or more eggs in the puncture. This operation gives rise to a spherical excrescence, known as nut-galls or Aleppo galls. The trade in nut-galls has considerably declined during the last few years, cheaper substitutes, such as sumach, myrobalans, &c., being now largely used in dyeing and printing.

*Chinese* or *Japanese Galls* are produced by a kind of fly (*Aphis Chinensis*) which punctures the leafstalks and branches of *Rhus semialata*, a small tree indigenous to Northern India, China, and Japan. Chinese galls are of a very irregular shape, and very light and hollow. They contain about 70 per cent. of tannin.

*Divi-divi* is the flat curved pods of *Caesalpinia coriaria*, a shrub growing in South America. They contain upwards of 50 per cent. of tannin.

*Myrobalans* are the fruit of different species of *Terminalia*, and chiefly obtained from *T. chebula*, growing in India. The tannin contained in them is, according to Stenhouse, not identical with that existing in galls.

*Sumach* consists of the powdered leaves and twigs of different species of *Rhus*, and generally obtained from *R. coriaria* or tanner's sumach, a shrub growing in Southern Europe. The best kinds come from Sicily or Spain, the others from Portugal and Italy. Sumach contains only 10 to 16 per cent. of tannin, which is the same as that found in galls.

Besides these drugs, there occur some others in commerce which also contain tannin, but they are of less importance. Amongst these may be named—*valonia*, consisting of the cups of a kind of oak (*Quercus Ægilops*) growing in Southern Europe; *Piedmontese galls* or *Knoppern*, growing on the acorns of *Q. pedunculata*; *Pistacia galls* or *Bokhara galls*, found on the leaves of a species of *Pistacia* in Asia; and *Bablah*, the pods of a plant imported from India.

Mineral and Pigment Colours—These colours, which are insoluble in water, are fixed on the fabric either mechanically or by chemical reactions. The fixing of them by mechanical means will be described later on; for the present it will suffice to describe the reactions by which the more important colours of this group are formed. They may be divided into three groups:—

(1) Oxides.
(2) Salts.
(3) Sulphides.

Oxides.—*Ferric Oxide*, $Fe_2O_3$, occurs in nature in a more or less pure state, and is obtained as a bye-product in the manufacture of Nordhausen sulphuric acid. Its colour varies from deep red to reddish-brown or brownish-purple. Red ochre is a mixture of clay and ferric oxide. *Ferric hydrate* is obtained as a brown precipitate by adding an alkali to a solution of a ferric salt or a ferrous salt. In the latter case the precipitate consists of ferrous hydrate, which in the pure state is white, but quickly by absorbing oxygen turns green, black, and then brown. The freshly-prepared ferric hydrate is $Fe_2(OH)_6$, but it readily loses water on drying, and is converted into $Fe_2O_3 + Fe_2(OH)_6$. This is also the composition of brown iron-ore and of rust. Yellow and brown ochres are mixtures of clay and the latter compound.

*Manganic Oxide*, $Mn_2O_3$.—When manganese sulphate or chloride is precipitated with potash and soda a white precipitate of *manganous hydrate*, $Mn(OH)_2$, is formed, which when exposed to the air quickly absorbs oxygen, and is converted into a deep brown manganic hydrate, which is known as *manganese brown* or *bistre*.

*Chromic Oxide*, $Cr_2O_3$.—On adding ammonia, or sodium carbonate, to a solution of green chromic chloride a greenish precipitate of chromic hydrate, $Cr(OH)_6$, is obtained, which on heating loses water, and is converted into the dull green chromic oxide.

A compound of both is *Guignet's green*, which is prepared by heating a mixture of red potassium chromate with boric acid and exhausting the melt with water. It forms a beautiful green powder, consisting chiefly of $Cr_2O_3 + Cr(OH)_6$, but which always contains a certain quantity of boric acid.

Salts.—*Lead Chromates.*—When a soluble salt of lead (acetate or nitrate) is added to a solution of yellow or red potassium chromate, a yellow precipitate is formed, consisting of *normal lead chromate* (*chrome yellow*), $PbCrO_4$. By acting with alkalies on this compound it loses chromic acid, and changes first into orange and then into a bright orange-red. *Chrome red* is also produced by adding chrome yellow to fused saltpetre; it is thus obtained as a bright red powder, consisting of $Pb_2CrO_5$ or $CrO_3 + 2PbO$.

*Chromic Arsenite.*—When precipitated chromic oxide is treated with a solution of sodium arsenite it acquires a bright green colour by combining with arsenious acid.

*Copper Arsenite*, $CuAs_2O_4$, or *Scheele's Green*, is simply obtained by adding a solution of copper sulphate to a solution of sodium arsenite, which is prepared by dissolving white arsenic (arsenous oxide) in caustic soda, or sodium carbonate.

*Emerald Green.*—This beautiful colour is a double salt of copper arsenite and acetate, and is readily obtained by boiling concentrated solutions of copper acetate and arsenious acid. A voluminous olive-green precipitate is first obtained, which on boiling is changed into a splendid green. It may also be obtained by boiling Scheele's green with acetic acid. The composition, as well as the shade of this body, varies according to the mode of preparation; but it appears that it principally consists of $Cu_2\begin{cases}(AsO_2)_3\\C_2H_3O_2,\end{cases}$ and is formed according to the following equation:—

$$4CuAsO_4 + 2C_2H_4O_2 = 2Cu_2\begin{cases}(AsO_2)_3\\C_2H_3O_2\end{cases} + H_2O + As_2O_3.$$

*Ultramarine.*—This beautiful blue pigment exists in nature as a mineral called *Lazulite*. It is obtained artificially by heating a mixture of China-clay, soda-ash, sulphur, and charcoal. The chemical nature of this body is not satisfactorily understood, and has given rise to almost as many discussions and researches as madder-root. All that is certainly known is, that ultramarine consists principally of a silicate of aluminium and sodium, combined with a sulphide of sodium. By the action of an acid it is decomposed, sulphur and silica separating out, while sulphuretted hydrogen is given off.

*Prussian Blue* is the compound of a radical which Liebig has called *Ferrocyanogen*, $Fe(CN)_6 = Cfy$. When a ferric salt is added to a solution of potassium, ferrocyanide (yellow prussiate of potash), a blue precipitate of *potassium-ferric ferrocyanide*, $Fe_2K_2(Cfy)_2$, is formed. This compound is insoluble in saline solutions, but dissolves freely with a beautiful blue colour in water. It loses its solubility, however, when heated above 110° C. Its aqueous solution is not changed by ferric salts; but by adding ferrous sulphate a deep blue precipitate of *ferrous-ferric ferrocyanide*, $2Fe_2Cfy_3 + Fe_2Cfy$, is produced. This body is the chief constituent of *Prussian blue*, which is prepared by precipitating prussiate of potash with commercial green vitriol (a mixture of ferrous and ferric sulphate), washing the precipitate in contact with air or with chlorine water, and then treating it with dilute hydrochloric acid, in order to remove oxide of iron or basic iron salts. The commercial product always contains potassium, and appears to be a mixture of the two compounds described above. It dissolves in oxalic acid with a fine blue colour. Alkalies destroy the blue colour, an alkaline ferrocyanide and ferric oxide being formed.

When hydrochloric acid is added to a solution of potassium ferrocyanide, a white precipitate of ferrocyanic acid, $CfyH_4 = Fe(CN)_6H_4$, is formed, which when exposed to the air absorbs oxygen with the formation of Prussian blue, while prussic acid escapes:—

$$5Fe(CN)_6H_4 + O = Fe_5(CN)_{12} + 18CNH + H_2O.$$

*Turnbull's Blue* is obtained as a deep blue precipitate by adding a ferrous salt to a solution of *red prussiate of potash* or *potassium ferricyanide* $K_6(C_{12}N_{12}Fe_2)$. This body is generally regarded as *ferrous ferricyanide*, $Fe_3(C_{12}N_{12}Fe_2)$. It has, however, the same properties and the same composition as Prussian blue, $Fe_5(CN)_{12}$; and there is every reason to believe that both bodies are identical. Its formation can be easily explained:—Ferricyanides are powerful oxidizing agents; thus, in acting on an alkaline solution of manganous oxide, the latter is converted into the peroxide, while the ferricyanide is reduced to a ferrocyanide. From this it appears highly probable, that the first action of potassium ferricyanide on a ferrous salt consists in converting a portion of the latter into a ferric salt. Thus we have now in solution together a ferrocyanide, and ferrous and ferric salts, which act on each other and form Prussian blue:

$$(1)\ K_6(C_{12}N_{12}Fe_2) + 3FeCl_2 + 2HCl = 2HK_3(CN)_6Fe + FeCl_2 + Fe_2Cl_6 + H_2O.$$

$$(2)\ 2HK_3(C_6N_6)Fe + FeCl_2 + Fe_2Cl_6 = Fe_3(C_{12}N_{12})Fe_2 + 6KCl + 2ClH.$$

The peculiar action of stannous salts in modifying the colour of Prussian blue, and producing a rich purplish blue, has never been explained.

Sulphides.—These colours have merely a historical interest. Two of them were formerly used in printing.

*Arsenic Trisulphide*, or *Orpiment*, $As_2S_3$, is found as a mineral, and is also formed by passing sulphuretted hydrogen through an acid solution of arsenic. It readily dissolves in ammonia; and on exposing this solution to the air, the ammonia volatilizes and orpiment is again deposited, and by this means it may be fixed upon cloth.

*Antimony Trisulphide*, $Sb_2S_3$, is obtained as an orange precipitate by acting with sulphuretted hydrogen on an acid solution of antimony. It is readily soluble in alkaline sulphides, and pre-

cipitated again by acids. On boiling it with soda and sulphur, and allowing the solution to cool, large yellow crystals of *sodium sulphantimonate*, $Na_3SbS_4 + 9H_2O$, crystallize out. This salt was formerly prepared for use in calico printing. When an acid is added to its solution, or when the latter is exposed to the air, a bright orange precipitate of antimony *pentasulphide*, $Sb_2S_5$, is obtained. The colour thus fixed on cloth was known by the name of "stinking orange."

MORDANTS.—This term is applied by dyers and printers to certain substances, which form with many colouring matters insoluble compounds. A mordant is in most cases first fixed on the cloth by impregnating the latter with a solution of the mordant, and then rendering the latter insoluble by chemical or physical means. Formerly it was believed that the action was purely mechanical, the mordant having a corrosive or biting action, which served to open the pores of the tissue, and thus allowed the colour to penetrate. From this notion the name was derived—*mordre* meaning, in French, "to bite."

It will not be necessary to describe the different mordants; their nature will be readily understood by remembering the chemical properties of the different colouring matters. It will be sufficient to state, that the mordants which are commonly employed are oxides or basic salts of heavy metals, such as aluminium, iron, tin (all being very weak bases), or compounds of such oxides with tannic acids. The practical dyer and printer uses the term mordant generally in a very indefinite sense, including any substance which facilitates the fixing of a colouring matter: thus, he calls even the solvent of a colour a mordant, if the former be not soluble in water.

In the dyeing of cotton the mordant is in most cases first fixed on the cloth; but as it must not only be deposited on the surface of the cotton, but be also contained in the interior of the fibre, it is first applied in solution, and then rendered insoluble by chemical decomposition.

How this is effected will be best understood by explaining the chemical operations which are employed in calico printing. We will therefore discuss this subject first, although it is much more complicated than that of simple dyeing.

CALICO PRINTING.—The different manipulations and processes of calico printing are almost as varied as the different kinds of patterns which are produced. They may, however, be divided into the following different styles, each of them being quite distinct from the other. By the combination of two or more any kind of pattern, however complicated, may be produced.

1. Dyeing on mordants.
2. Steam printing.
3. Spirit printing.
4. Colours fixed by oxidation.
6. Resist style
7. Discharge style.
8. Chemical printing.
9. Fixing by albumin.

While in dyeing or mordanting the substances are employed in a simple solution in order that they may penetrate the fibre completely, in printing it is required that only certain parts of the cloth shall be impregnated with the colour or mordant. Therefore a mere solution cannot be used for printing patterns, because it would spread out beyond the limits of its application, and this is avoided by the addition of certain substances, which are called *thickenings* or *thickeners*, such as gum or starch, which retain the solution of the mordant or colour within the desired limits.

The principal thickenings are flour, starch, and the different kinds of gum, as well as fats or oils. Mineral matters, such as pipe-clay, china-clay, &c., are also sometimes used for this purpose.

*Flour* is a mixture of starch and an albuminous substance called *gluten*. When wheaten flour is made into a paste with cold water, and after being tied up in a cloth is washed with water, the starch passes through, and gluten is left as a viscid elastic substance.

*Starch* or *Amylum* is widely diffused in the vegetable world, being found in nearly every plant. It is most abundant in grain, rice, Indian corn, potatoes; it exists also in large quantity in the stem of several palm trees, &c.

Under the microscope starch is seen to be made up of rounded granules, having an organized structure. The starch-granules of different plants vary much in form and magnitude, and can be easily distinguished from each other. An adulteration of better sorts of starch with cheaper ones can thus be readily detected.

Starch is insoluble in cold water; but heated with it to above 60° C. the granules burst, and a thick mucilaginous mass called starch paste is produced.

*British Gum* is obtained by heating wheaten starch to 150° C.; it is a white amorphous powder, which is perfectly soluble in water, forming a thick viscid solution. A cheaper sort is *calcined farina*, which is prepared in the same way from potato starch.

*Gum Arabic* is the product of several species of Acacia, growing in Western Asia, Nubia, Southern Egypt, India, &c., and occurs in commerce under different names, as *Senegal gum*, *Barbary gum*, *Talha gum*, &c. Natural gum is a compound of *arabin*, $C_6H_{10}O_5$, with potash, lime, and magnesia. Arabin is obtained by dissolving gum arabic in water, and acidulating the solution slightly with hydrochloric acid; on the addition of alcohol, arabin is obtained as a white amorphous precipitate. It may also be prepared by placing an acidulated solution of gum on a dyaliser, when the metallic chlorides will diffuse out, and leave a solution of pure arabin. Arabin having been dried, becomes insoluble even in boiling water, and only swells up. But when an alkali is added, it dissolves like ordinary gum.

*Gum Tragacanth* is an exudation from the stem of several species of Astragalus—low shrubs resembling our common furze, and growing chiefly in western Asia and Persia. It occurs in mammiform or vermicular masses, swelling up in water to a thick mucilage. So great is its power of absorbing water that, with fifty times its weight it forms a thick mucilage, which will only dissolve in a very large quantity of water. Starch, and the different kinds of gum, have the same percentage composition as cellulose, $C_6H_{10}O_5$.

DYEING ON MORDANTS.—This kind of work is also called the *madder style*, being chiefly used for madder colours. It may, however, also be applied for other vegetable and animal colours, which are soluble in water, and taken up from their solution by a mordant which has been previously fixed in the cloth. In order that the colours may appear in all their purity, the cloth must be first freed from all foreign matters which it naturally contains, as well as those which are imparted to it by the processes of spinning and weaving.

(1.) The first process to which the grey cloth is subjected is called *singeing*, its object being to remove the nap or the loose fibres on the surface of the cloth. This was formerly effected by drawing the cloth quickly over a red-hot bar of iron or copper; but now it is generally done by passing the cloth over a number of small gas flames, issuing from small holes bored in the upper surface of a hollow cylinder.

(2.) The cloth is next thoroughly wetted with water, which requires some time, because it always contains greasy matters, and therefore throws the water off. This point must be carefully attended to, for if it is not moistened throughout, the operations which follow will not proceed regularly. This second process is called *rot-steep*, because formerly the cloth was steeped in water until the size contained in it began to ferment and putrefy.

(3.) Next follows *liming*, or boiling the cloth in large boilers with milk of lime for twelve or sixteen hours. Thus the fat or grease contained in the cloth is saponified and converted into an insoluble lime-soap. After the cloth being pressed, it is passed through dilute hydrochloric acid, which removes any lime adhering to it, and at the same time decomposes the lime-soap and sets fatty acids free, which are easily removed by the next process.

(4.) After being washed with water the cloth is boiled in a solution of soda-ash and resin-soap. This is called *bowking*, and its object is to remove the fatty acids by converting them into a soluble soap.

(5.) After the cloth has been thus treated, it still contains some of the colour which is natural to it. It is therefore *bleached*, or first steeped in a clear solution of bleaching powder, and then passed through weak hydrochloric or sulphuric acid. After being well washed and dried it is ready for printing.

The mordants for madder-colours are *acetate of aluminium* or *red liquor*, which is obtained by decomposing aluminium sulphate with lead acetate and *ferrous acetate* or *iron liquor*, which is prepared by dissolving iron in pyroligneous acid. The former produces *madder-pinks*, and the latter the *purples* or *lilac*, which are the principal madder colours. Madder yields also strong reds and purplish-blacks by employing the mordants in a more concentrated state, while by using a mixture of them *chocolates* are produced, which, however, are not in much use, and generally replaced by *catechu-browns*.

Before the mordant is printed on the cloth, it is *thickened* with flour, British gum, &c., to which some *sightening* is added, *i.e.*, a decoction of Brazil wood for the reds, and logwood for lilacs and blacks. By this the pattern on the cloth becomes perceptible, and thus enables the printer to discover any irregularities which may occur. After printing the cloth is dried, and then *aged* or *stored*. The pieces are hung up in a large airy room, which is only warmed in winter. This exposure to the air has the effect of decomposing the mordants, acetic acid escapes, and the oxides of aluminium and iron are precipitated in the fibre. To hasten the process, as far as the iron mordant is concerned, some potassium chlorate is generally added.

The operation which now follows is a very singular one, and is called *dunging* or *cleansing*. The cloth after being printed always contains an excess of mordant which is not fixed, and if after ageing the cloth was immediately dyed, the non-fixed mordant would get loosened, and thus seriously interfere with the dyeing. No clear whites could be obtained, and the purity of the colours would be spoiled by the intermixing of the mordants. The excess of mordant cannot be removed by simply washing with water, because a portion of the fixed mordant would by removal of the thickening also get loose and might be deposited again partially in other parts of the cloth, and therefore the different mordants would again intermix and spoil one another. It is therefore necessary to have a liquid which is capable of removing the thickening and excess of mordant, and at the same time preventing any loose mordant fixing itself on the cloth. A liquid possessing these properties was found to be a mixture of hot water and cows' dung, and is in fact still the best material for this purpose. But besides the unpleasantness of working with such a body, the supply of it has fallen short since calico printing has reached such great dimensions. In certain localities printers had to keep their own cows simply for getting sufficient material. They therefore looked out for substitutes, and found them first in sodium phosphate and other phosphates; for these the arsenite, arseuate, or silicate of sodium, is now employed.

Cleansing plays an important part in dyeing on mordants; the heat of the liquor, as well as its strength, must vary with the different styles, and great care must be taken to have the operation done effectually. Dung substitutes are generally sufficient for iron mordants, but not for alumina; and therefore, in this case, printers generally finish the cleansing by wincing the pieces in cow dung before dyeing.

The action of cow dung has not been clearly explained. It contains a small quantity of alkaline phosphates, besides other salts, and also a peculiar albuminous substance which has been called *bubalin*, and to which some chemists ascribe its specific action.

After cleansing the cloth is washed and is then ready for the dye beck, which is prepared by mixing old ground madder with a sufficient quantity of water, but using not more than is required for the easy running of the pieces through the somewhat

gelatinous liquid. If too much water is used, the colour does not fix readily; on the other hand, if the quantity of water is too little, the brown and yellow colouring matters of the root, which are more soluble than alizarin, will be first precipitated by the mordant, and will thus prevent the fixing of the alizarin.

The dye beck is gradually heated to about 40° C., at which temperature the dyeing commences, and then the temperature is gradually raised to 80° C. The whole operation requires about two to three hours; because a certain quantity of alizarin is actually formed during the dyeing process, and further because it is but sparingly soluble in water, and that gone into solution must first be absorbed by the mordant before a fresh quantity can dissolve.

Printers have known for a long time that the brightest madder colours are produced if the water contains some lime. Rosenstiehl, who has carefully studied this subject, has found that this is due to the presence of carbonate of lime, which is kept in solution by carbonic acid. But as this gas soon escapes, a lime-lake of alizarin is precipitated. To prevent this, carbonic acid might be passed into the dye beck; this, however, is not convenient when working on a large scale; but the same good results are obtained from calcium acetate, which in the presence of alumina or iron oxide is completely decomposed, and the lime fixed with the colour. Alizarin even decomposes the nitrate and chloride of calcium, which is shown by the fact that by using these salts brighter colours are produced than by dyeing in distilled water alone; moreover, the bath becomes acid.

The power of alizarin to decompose salts is also proved by the steam colours, which are produced in presence of acetate, nitrates, chlorides, and sulphates.

Alizarin, which does not saturate mordants in distilled water, will do so completely if one equivalent of calcium acetate is present; but two equivalents give still better results, although one remains undecomposed; while three equivalents are less favourable, although the result is still superior to that produced by calcium carbonate.

Pseudopurpurin, which does not dye in the presence of one equivalent of calcium carbonate, fixes very well if one equivalent of calcium acetate is added; at the same time, some of it is converted into purpurin.

Purpurin saturates the mordants best if two equivalents of calcium acetate be present.

Madder extracts, and the artificial alizarins for red and purple, give the best results with two equivalents of the acetate; the bath is readily exhausted, and remains clearer than in using calcium carbonate.

If the value of madder extract or artificial alizarin has to be determined in the laboratory, it is convenient to use distilled water, to which the required quantity of a standard solution of calcium acetate is added. Certain dye-works, using hard waters, have for a long time improved them by adding acetic acid, which is quite rational. Waters containing large quantities of sulphates, chlorides, or nitrates, are also improved by the addition of calcium acetate, which decomposes these salts; and even sodium acetate may be used for this purpose; but an excess must be avoided, because a hot solution of this salt readily dissolves the colouring matters, and colours like an alkaline solution; but on cooling the colours again separate, showing that the salt is dissociated by heat. Whereas in using water containing calcium carbonate the dye-bath can be used for one operation only, the employment of the acetate allows it to be used for a number of times, if only from time to time equal equivalents of the colour and the acetate be added. At the same time, the colouring matter may be used in excess, and the dyeing will take place at a lower temperature, and more quickly.

The dyed goods are washed and boiled with soap and water to free the colours from the brown and yellow matters which are precipitated, and to clear the whites from any colour deposited on them. This operation is, however, generally not sufficient to get perfectly clear whites, which is effected by *chemicking* or wincing the goods in a dilute solution of bleaching powder, and then washing them carefully.

For very perfect work, in pink and red, some stannous chloride is added to the mordant, in order that any iron salt which may be present be prevented fixing together with the alumina. This solution is called tin-red liquor.

Alumina mordant may also be fixed by printing on the cloth a solution of alum in caustic soda (alkaline aluminate of soda), and then passing it through a solution of sal-ammoniac.

Instead of madder-root, garancin and similar preparations are often used; but lately artificial alizarin is much employed, either by itself or in conjunction with madder.

The following examples will give an idea in what proportions the mordants and thickeners are mixed, in order to produce the different colours or shades. The numbers represent either ounces or fluid ounces for liquids:—

*Pinks.*

| | *a.* | *b.* |
|---|---|---|
| Boiling water, | 610 | 760 |
| Acetic acid, of 11 Twaddle, | 30 | 400 |
| Red liquor, | 160 | 160 |
| Calcined farina, | 400 | 400 |
| Gallipoli oil, | 7½ | 7½ |
| Turpentine oil, | 7½ | 7½ |

The red liquor for these styles is prepared by treating 62½ parts of alum and 45 of brown sugar of lead with 200 of boiling water.

*Reds.*

| | Dark. | Middle. | Light. |
|---|---|---|---|
| Red liquor, of 12° Tw. | 100 | 100 | 100 |
| Water, | 100 | 400 | 1500 |
| Starch, | 24 | — | — |
| Calcined farina, | 6 | 200 | 600 |
| Gallipoli oil, | 3 | — | — |

*Lilacs.*

| | Dark. | Light. |
|---|---|---|
| Boiling water, | 960 | 960 |
| Iron liquor, of 11° Tw., | 120 | 30 |
| British gum, | 720 | 600 |
| Oil of turpentine, | 7½ | 7½ |

*Black.*

| | |
|---|---|
| Water, | 240 |
| Iron liquor, of 40° Tw., | 320 |
| Calcined farina, | 100 |
| Quercitron liquor, of 27° Tw., | 20 |
| Logwood liquor, of 25° Tw., | 20 |
| Olive oil, | 2½ |

The madder style is not confined to madder only, but there are several other colouring matters which may be applied to cloth in a similar way. The most important of these are:—

Quercitron gives with an alumina mordant a bright yellow, with an iron mordant an olive-grey, and with a mixture of both a number of yellowish olive shades. A good orange is produced by dyeing with a mixture of madder and quercitron on alumina mordants, and thus, by varying the proportions of the two dye-stuffs, various shades, from golden-yellow to scarlet, can be produced. By using as mordants different mixtures of red liquor and iron liquor, and dyeing with varying proportions of madder and quercitron, varying brown and fawn shades are obtained.

Logwood produces on iron mordants greys and blacks; and on alumina, violets and purples.

Cochineal yields on alumina a pinkish violet, and together with logwood fine lilacs; cochineal and quercitron dye on the same mordant a beautiful orange.

Besides these examples, a great number of others might be given; for by combining two or more colouring matters, and varying or mixing the mordants, an endless variety of shades can be produced.

Steam Printing.—*(a) Topical Steam Colours.*—This process is much more simple than the madder style. The thickened solution of the colouring matter is mixed with the mordant (when any is required), and printed topically on the cloth. After drying, the colour is fixed by heating the goods.

In this style neither dunging nor subsequent cleaning is required. Since the introduction of madder-extract and artificial alizarin, these substances are largely used in steam printing, by which very bright colours are obtained. The mordants are exactly the same as in the madder style, and are fixed along with the colour by steaming. The changes which take place are very simple; the acetates are decomposed by heat, and the colouring matter dissolves in the acetic acid which is set free. But by the continued action of heat the latter gradually escapes, and then the colour combines with the fixed mordant.

The following are a few recipes for thickenings, mordants, and different steam colours.

*Thickenings for Red.*

| | *a* | *b* |
|---|---|---|
| Wheat starch, | 60 | 60 |
| Water, | 200 | 170 |
| Acetic acid 8° Tw., | 40 | 170 |
| Gum tragacanth paste of 6 per cent. | 100 | — |
| Olive oil, | 15 | 15 |

*Thickening for Violet.*

| | |
|---|---|
| Wheat starch, | 50 |
| Water, | 180 |
| Gum tragacanth paste of 6 per cent. | 90 |
| Acetic acid of 8 Tw., | 30 |
| Olive oil. | 10 |

*Solution of Acetate of Alumina.*—34 lbs. of alum and 31 lbs. of soda crystals are dissolved, each separately in 40 gals. of water, and the solutions are mixed. The precipitate, consisting of basic sulphate of alumina, is well washed and pressed. 15 lbs. of the paste thus obtained is mixed with 6 lbs. of acetic acid of 11° to 12° Tw., and the mixture heated to 32° C., until the precipitate is dissolved, and then the solution is filtered.

*Solution of Nitrate of Alumina.*—This mordant, which is also much used for steam colours, is obtained by dissolving 10 lbs. of nitrate of lead, and 10 of alum in 10 gals. of boiling water, allowing the precipitate to settle, and then decanting the clear liquid.

Steam Reds.

(*a*) 80 oz. of alizarin paste of 15 per cent., or 120 of 10 per cent., are well mixed with 100 fluid oz. of acetic acid of 8° Tw.
200 oz. of water.
20 oz. of olive oil.
20 oz. of acetate of lime of 14° Tw. ; and
50 oz. of wheat starch.

The mixture is boiled, and when cold, 20 oz. of acetate of alumina are added.

(*b*) 260 oz. of alizarin paste, 15 per cent.
60 oz. of acetate of alumina, 17° Tw.
30 oz. of nitrate of alumina, 22° Tw.
40 oz. of acetate of lime, 24° Tw.
1000 fluid oz., thickening for red.

(*c*) *Very dark red.*

360 oz. of alizarin paste.
60 oz. of acetate of alumina.
40 oz. of nitrate of alumina.
50 oz. of acetate of lime.
1000 oz. of thickening.

(*d*) *Steam red without oil.*

280 oz. of alizarin paste.
480 oz. of acetic acid, 11° Tw.
180 oz. of farina.
240 oz. of water.

Boil, and add when cold—

48½ oz. of acetate of lime, 22° Tw.
100 oz. of nitrate of alumina, 20° Tw.
150 hyposulphite of lime, 270° Tw.

(*e*) *Pink.*

160 oz. of alizarin paste.
800 oz. of water.
50 oz. of acetate of alumina, 17° Tw.
25 oz. of acetate of lime, 24° Tw.
2000 to 3000 oz. of thickening.

*Lilac.*

90 oz. of alizarin paste.
1000 oz. of water.
20 oz. of iron liquor, 17° Tw.
37 oz. of acetate of lime, 22° Tw.

The pieces are well dried, and steamed with moist steam for 1 to 2 hours; then they are aged for a day or two, and now passed during 1 to 2 hours through a bath containing—

100 oz. of water.
2 oz. of chalk.
½ oz. of arsenate of soda.

After washing, the pieces are soaped.

Steam printing was formerly chiefly employed for wood colours, which yield very permanent and brilliant shades.

Before printing, oxide of tin is generally fixed on the cloth by padding it in a solution of sodium

stannate, and then passing it through a solution of sal-ammoniac. By the presence of tin oxide the brilliancy of most steam colours is much increased. The mordant which is most frequently used is red liquor, to which some oxalic acid or some other acid is added, to prevent a precipitation of the colouring matter with the mordant. The principal colours obtained in this way are the following:—

*Steam red* is obtained by using a mixture of decoction of cochineal, stannous chloride, and oxalic acid. The carminate of tin which is thus formed is a very brilliant colour. Cheaper but less brilliant reds are produced by using extract of Brazil wood. The following receipt yields a very good red:—10 lbs. of extract of cochineal, of 6° Tw., are boiled with 1 lb. of starch, and the warm paste is mixed with 3 oz. of oxalic acid and 4 oz. of tin crystals.

*Steam yellow* is generally produced by employing a decoction or extract of Persian berries; but fustic or quercitron may also be employed, the mordants being red liquor or alum, with some tin crystals.

(*a*) 10 lbs. of extract of quercitron, of 7° Tw., are mixed with a solution of 1 lb. of alum in 2½ lbs. of water, and thickened with 3½ lbs. of gum Senegal.

(*b*) 10 lbs. of extract of Persian berries, standing at 8°, is mixed with 20 oz. of alum, 3 lbs. of gum, and a small quantity of tin crystals.

*Steam purple* is obtained by using extract of logwood and red liquor.

*Steam black* is also a logwood colour, a decoction or the extract of this wood being used, mixed with iron liquor, red liquor, and some acetic acid, to which sometimes a little oil is added. The following recipes may serve as examples:—

(*a*) *Black.*

| | | |
|---|---|---|
| Logwood extract, of 8° Tw., | 5 | lbs. |
| Acetic acid, | 1¼ | " |
| Acetate of alumina, of 14° Tw., | 1¼ | " |
| Iron liquor, of 20° Tw., | 1¼ | " |
| Starch, | 3 | " |

(*b*) *Pluish black.*

| | | |
|---|---|---|
| Logwood extract, 5° Tw. | 2 | gals. |
| Starch, | 7 | lbs. |

Boil, and add—

| | | |
|---|---|---|
| Chlorate of potash, | 1½ | oz. |
| Pink salt, | 4 | lbs. |

(*c*) *Lilac.*

| | | |
|---|---|---|
| Logwood extract, 14° Tw. | 8 | gals. |
| Water, | 48 | " |
| Gum, | 17 | lbs. |
| Alum, | 4 | " |
| Nitrate of copper, of 78° Tw., | ¼ | " |

(*d*) *Grey.*

| | | |
|---|---|---|
| Logwood extract, 1° to 2° Tw., | 4 | lbs. |
| Acetic acid, 12° Tw., | 4 | " |
| Copperas, 30° Tw., | 4 | " |
| Gum water, 30° Tw., | 120 | " |

*Aniline Colours.*— Rosaniline and its derivatives are also employed as steam colours. All these bodies form with tannic acid insoluble coloured compounds, and may therefore be fixed by simply printing a mixture of the colour with acetic acid and tannin, and steaming.

The colours thus obtained are very bright, but also very fugitive. They become faster if a metallic oxide, or any substance forming with tannic acid an insoluble compound, be present. The following methods have therefore been proposed:—

(*a*) The steamed goods are passed through a warm solution of tartar emetic (LLOYD & DALE'S patent).

(*b*) The cloth is impregnated before printing with stannic oxide or alumina.

The cloth is printed with tannic acid, and after steaming passed through a solution of gelatin or tartar emetic, and then dried in a bath acidulated with acetic acid.

Soluble aniline-blue or alkali-blue is readily fixed by mixing it with aluminium acetate and steaming the cloth after printing.

Another method for fixing aniline colours, which has come into use lately, has been objected to, because the cloth is impregnated with a considerable quantity of arsenic. Arsenous acid (white arsenic) is dissolved in glycerin, and this solution is mixed with red liquor and the colour. The thickened mixture is printed, dried, and steamed. The mordant in this case is an arsenite of alumina, which is quite insoluble in water.

The process of PERKIN and SCHULTZ is similar and gives excellent results; a good bluish-pink being obtained by printing a thickened mixture of 1 litre of aluminium acetate of 10° B., 80 grammes of sodium arsenite, and 16 grammes of magenta. The pieces are then steamed for an hour, soaped, and well washed. Nearly all the aniline colours may be fixed by this process.

*Saffranine* may be fixed by boiling a mixture of aluminium acetate 1 gallon, water 1 gallon, and starch 2 lbs.; when cold, 1 pint of arsenic solution is added, and the goods after printing are steamed for half an hour. The solution of aluminium acetate is prepared by dissolving 5 lbs of alum in 2 gallons of water, precipitating with 6 lbs. of lead acetate, and allowing to settle. To obtain the arsenic solution, 4 lbs. of white arsenic is dissolved by heat in 1 gallon of glycerin.

*Annotto* is also much used for obtaining deep yellow steam colours, which are best produced by the following process:—

13 lbs. of annotto are mixed with 2·4 gals. of spirits of wine of 90 per cent., and 2·4 gals. of boiling water and 1·2 gal. of soda-lye of specific gravity 1·16 are added. The mixture is allowed to stand over night, and the clear liquid is then decanted. The residue is well pressed, and then exhausted with 3·6 gals. of boiling water, and the solution allowed to settle. All the clear liquids thus obtained are mixed and thickened by adding 6 gals. of tragacanth paste, containing 3·5 per cent. The goods are printed, steamed, and washed. If lighter shades be required, extract of berries and alumina acetate are added.

*Chemical Steam Colours.*— The most important colour of this group is *Prussian blue*, which is obtained by means of a mixture of potassium ferrocyanide

and an acid such as tartaric, oxalic, or sulphuric acids. The chemical reaction taking place on steaming the goods is very simple: the acid sets free ferrocyanic acid, which, as we have seen, is decomposed by the action of heat and the air into prussic acid and Prussian blue.

*Steam Blue.*—A solution of 6½ lbs. of yellow prussiate is dissolved in 10 lbs. of water, and mixed with a solution of 3⅓ lbs. of alum, 2½ of oxalic acid, and 2½ of tartaric acid. After adding a little nitrate of iron for "sightening," the mixture is thickened with gum.

A very good *steam green* is obtained by employing a thickened mixture of extract of Persian berries, potassium ferrocyanide, stannous chloride, alum, and oxalic acid. The formation of a green colour under these conditions does not require any further explanation.

By using a combination of the madder style with steam colours, a great variety of colours may be obtained. Thus, a design in black, lilac, pink, green, blue, orange, and yellow, on a white ground, may be obtained by first printing on the cloth two iron liquors of different strength, one for black and the other for lilac, and with red liquor for pink. After being aged and dunged, the cloth is dyed with madder and then printed with the mixture for steam blue and steam yellow, which latter is also printed on a part of the pink to produce orange, while the green results from the mixture of the blue with the yellow.

SPIRIT PRINTING.—This style has derived its name from the fact that stannic chloride was the mordant originally employed for this kind of work. Anhydrous stannic chloride is a fuming volatile liquid, and was therefore formerly called *spirits of tin*, or *dyers' spirit*. It is generally prepared by dissolving metallic tin in a mixture of hydrochloric and nitric acid, care being taken to avoid too great an elevation of temperature. The vegetable colours which are applied to the cloth are soluble in a strong solution of the mordant, but precipitated together with the mordant on the addition of water. Therefore, on printing the colour together with the mordant on calico, and then, after being dried in a cool place and passing the pieces through water, the colour is fixed.

At present all fugitive topical colours which are not fixed by steaming are called *spirit or fancy colours*. The following are the more important of this class:—

*Spirit Purple.*—A decoction or extract of logwood is mixed with tin spirits and starch paste and printed on the cloth, which is dried for two days in a warm room, and then washed. By using peachwood, &c., *spirit pinks* are obtained.

*Spirit Purple.*—1 gal. of logwood liquor, of 6 Tw., is boiled with 1 lb. of starch, and after it is almost cold it is mixed with 1¼ pint of tin spirits, of 120° Tw., and ¼ pint of oil.

*Spirit Pink.*—1 gal. peachwood liquor, at 8° Tw., 1¼ lb. starch; boil, and add ¼ pint solution of nitrate of copper, at 100° Tw.; and when the mixture is almost cold, 4 oz. of pink salt, ½ pint of oil, and 1½ pint of spirits of tin are added.

*Spirit Yellow* is produced by Persian berries, the mordant being either tin spirits only or mixed with alum. A mixture of red liquor and alum may also be used.

*Spirit Black.*—Extract or a decoction of logwood is mixed with ferric nitrate (pernitrate of iron) and ferrous sulphate or copperas. This mixture thickened with starch may be printed on the cloth at the same time as the mordants for madder style, because after ageing the colour becomes so fast that it is but little affected by the subsequent operations of dunging, dyeing, and clearing.

*Examples of Spirit Black.*

| No. 1. | No. 2. |
|---|---|
| 1 gal. of decoction of logwood, at 7° Tw. | 1 gal. of logwood liquor, at 8°. |
| 4 oz. of copperas. | 2 oz. of copperas. |
| 1 lb. of pernitrate of iron, at 50° Tw. | 1 pint of pernitrate of iron. |

Boil the logwood liquor and copperas with 1¼ lb. of starch, and when almost cold add the pernitrate.

A fast black is also obtained by printing with a mixture of logwood extract, red liquor, and oxalic acid, and passing the cloth after ageing through a solution of red potassium chromate. By using more dilute solutions, chocolate or puce colours are produced. This colour is a combination of the colouring matter of logwood (hæmatein) with chromic oxide. These older blacks are now generally superseded by aniline black, which will be described in the following chapter.

*Colours fixed by Oxidation.*—The most important colours of this style are *catechu brown*, *indigo blue*, and *aniline black*.

*Catechu Brown.*—Catechu contains no real colouring matter, but under the influence of oxidizing agents it developes a fine and very permanent brown or chocolate, which is often applied in conjunction with madder colours. The mordants for this style are copper salts, the nitrate being chiefly employed, which, while oxidizing the catechu, are reduced to salts of the suboxide. But as the latter are insoluble in water, they would fix on the cloth and thus prevent a complete oxidation. It is therefore essential to keep them in solution, which is easily done, by mixing the copper salt with sal-ammoniac. This mixture is printed together with the madder mordants, the colour being developed by ageing, and not affected by the processes of dunging and clearing.

Bichromate of potash is also frequently used as an oxidizing agent.

(*a*) *Dark Catechu Brown for Madder.*—6 lbs. of catechu are boiled with 1 gal. of water and 1¼ lb. of sal-ammoniac, and to the strained decoction are added 2 gals. of gum water, 2 pints of nitrate of copper of 80°, and 1½ pint of a solution of acetate of copper, which is prepared by dissolving 4 lbs. of sugar of lead, and 4 lbs. of sulphate of copper in one gal. of warm water.

(*b*) *Medium Brown.*—5 lbs. of catechu, 12 oz. of sal-ammoniac, 4 pints of water; boil, strain, and add 1 lb. of acetate of copper, and 1 gal. of gum water.

(*c*) *Chrome Brown.*—6 lbs. of catechu are boiled with 4 lbs. of water and 12 lbs. of acetic acid at 10°; the solution thickened, printed, steamed; and then the

cloth is passed through a hot solution of bichromate of potash, containing ½ per cent. of the salt.

INDIGO PRINTING.—The chemical theory of this style is simple enough. Finely ground indigo is mixed with a reducing agent, and the mixture is printed on the cloth, which is dried and then dipped into an alkaline solution. Thus the indigo blue is reduced to soluble indigo white, which penetrates the fibre, and is precipitated by passing the goods through a weak acid. On now exposing them to the air, the indigo white is oxidized again to indigo blue.

The china blue style, which has derived its name from the colour resembling the blue on old china, was formerly always employed to produce two or more different shades on a white ground. This is done by printing a thickened mixture of finely ground indigo and ferrous sulphate or acetate of different strength, and after drying, dipping the cloth alternately (1) into milk of lime; (2) into a solution of ferrous sulphate; (3) into caustic soda. By these operations the blue is gradually reduced and absorbed by the fibre. The ferrous oxide which is produced by the subsequent immersions can only act on the indigo which is on the surface of the cloth, and thus on continuing the dippings, more and more indigo-white is deposited within the fibre. During these operations the whole surface of the cloth becomes coated with oxide of iron, which is removed by dipping in a dilute acid.

The following method is given by THILLAYE.

16 lbs. of indigo, 4 lbs. of orpiment, 22 lbs. of copperas, and 100 lbs. of water are well ground together for three days, the water being added only gradually. This gives an almost black colour; to obtain the different lighter shades, it is mixed with gum water. Thus twelve different shades are obtained by diluting it in the following proportions:—

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Volume of normal colour, | 1 | 11 | 10 | 8 | 6 | 4 | 2 | 2 | 2 | 2 | 2 | 2 |
| Gum water,..... | 0 | 1 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 | 20 |

After printing, the cloth is hung in a warm room for two or three days, and then alternately passed through the following solutions.—

(1) *Lime vat*, consisting of 100 lbs. of quicklime in 600 gals. of water.

(2) *Iron vat* is a solution of ferrous sulphate of spec. grav. 1·048.

(3) *Soda vat*, or caustic soda of spec. grav. 1·055.

The pieces are left in each vat for 10 minutes, and are dipped in the following order:—

| | | |
|---|---|---|
| Lime vat. | Soda vat. | Lime vat. |
| Iron vat. | Iron vat. | Iron vat |
| Lime vat. | Lime vat. | Soda vat. |
| Iron vat. | Iron vat. | |

The mixture used by Lancashire printers is different. PARNELL gives the following proportions:—

Indigo, 16 lbs.
Strong iron liquor, from 5 to 6 gals.
Orpiment, 2 lbs.
Gum water, sufficient to make 8 gals.

To obtain the different shades, it is diluted in the following proportions:—

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Vol. of normal colour, | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Vol. of gum water,... | 0 | ½ | ¾ | 1 | 2 | 3 | 5 | 7 | 9 | 12 | 16 |

The part which orpiment (arsenic sulphide) plays in the production of China blue is not known. As it reduces indigo only at a boiling heat, it appears that as good a colour is produced by leaving it out; PERSOZ recommends the following proportions:—

| | | | |
|---|---|---|---|
| Indigo,..... | 17½ lbs. | Gum,..... | 33 lbs. |
| Copperas,... | 17½ " | Water,..... | 55 " |

Orpiment may, however, also be used without a ferrous salt for producing a good *pencil-blue* by proceeding as follows:—

20 gals. of caustic potash, at 34° Tw.; 12 gals. of finely ground indigo paste, containing 3¾ lbs. per gal., are boiled, and 22 lbs. of orpiment are gradually added. When boiled for an hour, 2 gals. of caustic potash, at 20° Tw., are added; and after standing for two hours, the clear liquid is thickened with gum Senegal and a little oil of turpentine.

Instead of using a ferrous salt or orpiment, zinc dust, finely-powdered tin, or stannous oxide, may be used as reducing agents.

A different method of indigo printing is the following:—

Finely ground indigo is reduced by heating it with caustic soda and tin crystals. On adding hydrochloric acid to the solution, a compound of indigo white and stannous oxide is precipitated. This *indigo precipitate* must be quickly washed and thickened. On dipping the cloth in milk of lime, indigo white is set free and fixed by exposure to the air, and dipping in dilute sulphuric acid to remove the lime. A fast green is obtained by adding to the mixture a soluble lead salt; which is first converted into the oxide, and then into the sulphate. It is now only required to pass the cloth through potassium chromate to obtain the desired green.

Another powerful deoxidizing agent, which has lately come into use for indigo printing, is sodium hydrosulphite, $HNa_2SO_3$. This salt, which is obtained by the action of zinc on a solution of acid sodium sulphite, reduces indigo blue rapidly in the cold to indigo white, which dissolves in presence of an alkali. The thickened solution is printed on the cloth, and the colour developed by exposure to the air and dipping in a solution of potassium dichromate.

SCHÜTZENBERGER and LALANDE give the following proportions:—1 lb. of finely ground indigo is mixed with sufficient water to hold it in suspension, and with from 3 to 8 lbs. of hydrosulphite of sodium, and the same or a sufficient quantity of caustic soda or potash.

*Aniline Black.*—It has already been stated that in the manufacture of mauve from aniline a large quantity of a black insoluble substance is formed. This aniline black can also be produced by oxidizing an aniline salt with which cotton has previously been impregnated, and thus a very fast colour is produced.

Aniline black was first applied to calico by JOHN LIGHTFOOT of Accrington; according to his original patent a mixture of aniline hydrochloride, potassium

chlorate, chloride or sulphate of copper, and sal-ammoniac or an organic acid, is printed on the cloth, which is then aged and passed through a solution of potassium chromate.

This process, however, was soon given up, because the mixture attacked the copper rollers and weakened the cloth. Several other processes were subsequently patented, the first great improvement being effected by M. Cordillot, who replaced the salts of copper by ammonium ferricyanide. This process, however, is expensive, and does not produce such a good black as Lightfoot's method. M. Lauth, therefore, endeavoured to improve the latter, and succeeded completely. Instead of a copper salt he used precipitated copper sulphide, which is printed together with aniline hydrochloride, potassium chlorate, and sal-ammoniac.

The sulphide of copper is obtained by precipitating a solution of copper sulphate with potassium sulphide: 150 grms. of the washed and moist precipitate are mixed with 500 grms. of starch and 250 grms. of water, and this mixture is then added to another mixture, which is composed of—

| | |
|---|---|
| Tragacanth paste, | ½ litre. |
| Calcined farina, | 650 grms. |
| Water, | 950 " |
| Chlorate of potash, | 150 " |
| Sal-ammoniac, | 50 " |
| Aniline hydrochloride, | 400 " |

The following two mixtures produce also a good black:—

(1) 14 gals. of water.
26 lbs. of starch.
11 lbs. of British gum.

Boil and add—

9 lbs. of chlorate of potash.
4½ lbs. of sal-ammoniac.
6½ lbs. of sulphide of copper.

Allow to cool and then add—

9 lbs. of aniline.
11 lbs. of tartaric acid.

After printing, age for three days at 33° to 35° C., pass through a weak solution of soda crystals, and soap the yarn at 80° C.

(2) 9 galls. of water.
9 lbs. of starch.

Boil and add—

2 lbs. of chlorate of potash.
2½ lbs. of sal-ammoniac.
4 lbs. of sulphide of copper.

Mix and add—

10 lbs. of aniline hydrochloride.

Hang for a day or two and wash.

*Aniline greys* are produced by a similar process; thus, the following proportions yield a good silver grey:—

| | |
|---|---|
| Gum water, | 1 gal. |
| Chlorate of potash, | 5 ozs. |
| Sal-ammoniac, | 2½ " |
| Sulphide of copper, | 7½ " |
| Aniline, | 5 ozs. |
| Tartaric acid, | 15 " |

A darker grey is obtained by using—

| | |
|---|---|
| Gum water, | 1 gal. |
| Chlorate of potash, | 10 ozs. |
| Sal-ammoniac, | 5 " |
| Tartrate of chromium, | 25 " |
| Aniline, | 2½ ozs. |
| Tartaric acid, | 15 " |

The tartrate of chromium is produced by dissolving 40 ozs. of bichromate of potash in 1 gal. of water and adding 60 ozs. of tartaric acid.

Lucas' soluble black, which is principally a mixture of copper acetate and aniline hydrochloride, is also used in printing. The liquid black mass is thickened and printed, and the goods are, after being exposed for some days to the air, passed through a dilute solution of soda ash.

John Lightfoot tried also the action of other metallic salts on aniline, and found that among others, the salts of iron, uranium, erbium, and vanadium produce good blacks. At that time (1871), however, vanadium and its compounds were so extremely rare, that nobody could dream of using them for printing. But lately deposits of a vanadium ore have been discovered in Shropshire, from which pure vanadium compounds are prepared on a large scale by the Magnesium Metal Co., near Manchester, who supply it at a price and in sufficient quantities to make it commercially available. The advantage which vanadium has over copper sulphide is, that its compounds are much more stable, and one part will go as far as 200 to 300 parts of the sulphide. Moreover, the process becomes much more simple; it is only necessary to dissolve aniline hydrochloride and chlorate of soda in water, and add to the thickened solution a little vanadic acid in powder.

The quality and peculiar shade of the black depends very much on the kind of aniline which is employed. Pure aniline gives, according to Hartmann, a very brilliant black, while magenta-auiline and pseudotoluidine yield a bluish-black, and the solid toluidine only a dirty brown.

When naphthylamine is used in the place of aniline, a violet is produced. The following proportion has been recommended by a printer:—

| | |
|---|---|
| Naphthylamine, | 8½ oz. |
| Hydrochloric acid, | 5½ oz. |
| Water, | 7 lbs. |
| Starch, | 2 lbs. |
| Water, | 4 lbs. |
| Tragacanth paste containing 3 oz., | 2 lbs. |

Boil, mix the two solutions, and when cold, add a solution of 460 grains of chlorate of potash in 2 lbs. of water.

Resist Style.—The object of this style is to produce a white design on a coloured ground. This is effected by first topically printing on the white cloth a substance which is called *resist* or reserve, and possesses the property of preventing the colour from fixing when the cloth is afterwards dyed. Resists may act either mechanically or chemically.

(1) *Fat resists.*—A white pattern on a lilac ground may be obtained by first printing on the cloth a resist consisting of a mixture of suet and gum water, and then padding with weak iron liquor, which of

course does not penetrate the parts which are covered with the resist. The cloth is now aged, dunged, dyed, and cleared. On the white pattern which is thus obtained different steam colours may be printed.

(2) *Resists for Mordants.*—These resists are chiefly employed in madder style, to produce white dots or other patterns on lilac or pink, &c. This is easily effected by printing on the mordants lemon juice or citric or tartaric acids, which combine with the alumina or oxide of iron, and form soluble salts, which are not decomposed by ageing and dunging.

Another resist for iron mordant is stannous chloride, which, as we have seen, is also used for preventing any oxide of iron from being deposited on the alumina mordant, in order to obtain very bright pinks and reds. If therefore stannous chloride is mixed with red liquor, well defined red designs surrounded by purple or lilac are obtained.

(3) *Resists for colouring matters* are almost entirely used for producing white patterns on indigo blue. The substances used for this purpose are principally copper salts, such as the sulphate and acetate, which are thickened and mixed with soap and lard, and printed on those parts of the cloth which have to remain white. After being dried, the cloth is dipped in the indigo vat, which is prepared by mixing together a solution of ferrous sulphate with finely ground indigo and slacked lime. Thus a solution of indigo white is obtained, which is absorbed by the cloth, and on exposing it to the air, takes up oxygen, and thus insoluble indigo blue is deposited in the fibres. By repeating this process, and using vats of different strength, any indigo blue shade may be obtained on the cloth, excepting on those places where the resist has been applied. The indigo white is not in this case absorbed, partly on account of the grease, but chiefly from the chemical action of the copper salt, which by dipping in the vat is changed into copper hydrate, which exerts an oxidizing action on the indigo white; indigo blue being precipitated before the solution can reach the fibre. The colour is therefore only attached to the resist, and is easily removed by washing.

Discharge Style.—This style resembles the resist style, in so far as its object is to produce white patterns on a coloured ground, but differs from it by the *discharge* being only applied after the cloth has been dyed. The materials used as discharges are chiefly oxidizing agents, such as chlorine, chromic acid, &c.

Thus, to obtain a white pattern on an indigo-blue ground the dyed cloth is padded with a weak solution of potassium dichromate, and carefully dried in the cold and dark. It is next printed with tartaric or oxalic acid. Free chromic acid is thus formed, which at once oxidizes and destroys the blue. By mixing the discharge with a lead salt, lead chromate is formed, and a yellow pattern on a blue ground is thus produced.

A mixture of potassium ferricyanide and caustic soda also discharges indigo completely.

Potassium dichromate cannot be used as a discharge for other colours, because it injures them by its oxidizing action. To discharge madder colours, a solution of tartaric acid or arsenic acid is thickened with gum and pipe-clay and printed. After the cloth has been suspended for a day or two, it is passed through a weak solution of bleaching powder, and then well washed. Bleaching powder acts on madder colours and other fast colours very slowly; but on the parts of the cloth where the acid has been applied free chlorine is liberated, and acts instantaneously on the colour.

Prussian blue and mineral colouring matters may also be discharged by chemical reactions, as we shall see under the next heading.

Chemical Printing.—The chemical principles which are involved in this style are so very simple, that it will be only necessary to illustrate them by the following examples:—

*Prussian Blue.*—To dye the whole surface of a piece of cloth with this colour it is padded in a solution of acetate or sulphate of iron, or a mixture of both, and then, after being dried, winced in chalk and water. It is next winced in a solution of potassium ferrocyanide, which is slightly acidulated with sulphuric acid. If a blue design is required the cloth is printed with a thickened iron solution (acetate or sulphate), aged, winced in chalk and water, and dyed in an acidulated solution of potassium ferrocyanide.

The formation of Prussian blue is easily explained. By the processes of ageing and winding in chalk and water, ferric oxide is deposited in the fibre, and this, by the action of the acid and the ferrocyanide, is then converted into Prussian blue.

If a white figure is required on a ground of Prussian blue it is printed with a paste containing caustic potash, and then passed through a solution of oxalic acid. The alkali converts the Prussian blue into soluble ferrocyanide and oxide of iron, which is dissolved by the oxalic acid.

*Chrome Yellow and Orange.*—A piece of cloth is dyed with chrome yellow by first padding it with a solution of lead acetate, and after drying passing first through a weak solution of sodium carbonate and then through a solution of potassium dichromate.

To print this colour a thickened solution of lead acetate or nitrate is first printed on the cloth, which after drying is treated as above.

*Chrome Orange* is obtained by boiling the cloth in lime water, after it has been dyed or printed with chrome yellow. A chrome yellow pattern on orange ground is produced by printing an acid on the orange, while greens are obtained by first applying a mixture of iron liquor and lead acetate, and then wincing in an acidulated solution of yellow prussiate and bichromate of potassium.

Another style of green is produced by printing a mixture of lead nitrate and indigo precipitate (the compound of stannous oxide and indigo white), fixing by passing through a solution of sodium carbonate, and dyeing in potassium dichromate.

*Bistre, Manganese Brown or Bronze.*—To obtain this colour the cloth is padded with a solution of manganese chloride, and after drying passed through

a strong cold solution of caustic soda to precipitate manganous hydrate, which is oxidized to the brown oxide, either by exposing the goods to the air, or by dipping them into a solution of bleaching powder.

A white design on brown ground is produced by printing on bistre a solution of stannous chloride, by which the brown oxide is reduced to manganous chloride, which is readily removed by washing. The brown is also discharged by most acids, and therefore by using certain acid mordants the oxide of manganese is removed, while the mordant becomes fixed, and may then be dyed in the usual way. In this way a great variety of coloured designs on a brown ground can be produced.

*Iron buff* consists of ferric hydrate, and is obtained by padding or printing either with ferric nitrate or a mixture of ferrous acetate and sulphate (*buff liquor*), ageing, and passing through milk of lime or caustic soda. When after ageing a mixture of oxalic and tartaric acids is printed on the cloth, the iron is discharged, and thus white patterns on a buff ground are formed.

Colours fixed by Albumin.—The fixing of pigment colours by albumin is a merely mechanical process. Commercial albumin is obtained from blood by removing the coagulum, and evaporating the clear serum at a moderate temperature. Egg albumin is also sometimes used, and consists of the dried white of eggs.

Good albumin is perfectly soluble in water at the common temperature, but becomes insoluble or coagulates above 70° C. Therefore on mixing its solution with a pigment colour and starch paste or tragacanth, printing the mixture on cloth and steaming it, the albumin coagulates and incloses the pigment in the fibre so firmly that the colour becomes permanently fixed. The principal pigment colours which are fixed in this way are ultramarine, Guignet's green, emerald green, chrome yellow, orange and red, iron ochres, &c.

Albumin is also used for printing aniline colours, but then it acts not only mechanically but also chemically, because all substantive colours have the same affinity for albumin as for wool and silk. Such colours are therefore permanently fixed by mixing them with a solution of albumin and gum, printing the mixture in the usual way, and steaming the goods. In the place of albumin glue may be used, which is boiled with 20 parts of water, and to this solution so much potassium dichromate is added that the liquid becomes straw yellow. In this solution the colour is dissolved; and after thickening with starch or gum it is ready for printing. Goods thus treated do not require steaming, the colour being fixed by exposing the goods to sunshine.

To print with aurin and peonin the colour is mixed with magnesia or oxide of zinc and a solution of albumin. In this case the colour forms with the oxides insoluble lakes, and may therefore be also fixed by using a mixture of gum water and glycerin in the place of albumin.

The Dyeing of Cotton.—In the dyeing of cotton, as well as in that of other fabrics, great care must be taken to avoid an uneven or patchy coloration. To do this, two conditions must be carefully fulfilled; (1) The goods must never be dipped into the dye beck in the dry state, but must be completely moistened with water. (2) They must be always moved about in the bath, in order to avoid a partial exhaustion of a portion of it.

If in the following recipes weights or measures are given, they are intended for 10 lbs. of yarn or cloth.

(1) *Colours not requiring a Mordant.*—The number of substantive colours which can be fixed on cotton without the intervention of a mordant is but small.

*Safflower* was, before the discovery of the aniline colours, used for dyeing on cotton delicate rose and pink tints. For this purpose an alkaline solution of crude carthamic acid is slightly acidulated with citric acid, and the cotton steeped in it until it has acquired the desired shade.

*Annotta* is fixed on cotton by dissolving it in a hot solution of soda crystals, steeping the goods in the liquid for twenty minutes or longer, pressing them, and washing in slightly acidulated water. Better results are, however, obtained by first impregnating the cotton with tannate of tin. It may also be fixed by the same method which is used for steam printing.

(2) *Dyeing on Mordants.*—Most substantive colours and, of course, all adjective colours can be fixed on cotton only by the intervention of a mordant, with which the yarn must first be impregnated before it is passed into the dye beck. Some substantive colours will, however, dye on non-mordanted cotton very pales shades, so-called tint shades.

*Aniline Colours.*—Aniline red, as well as its coloured derivatives, are readily fixed on cotton by first saturating it with tannin. For fine work a solution of tannic acid is used, while for common work a decoction of sumach or of other astringent substances is employed. After the cotton has been thoroughly saturated, it is wrung out, and now passed through a warm solution of tartar emetic. According to the shade required, these processes are repeated once or more. The dyeing may be performed in a cold or warm solution of the colour.

Another good mordant for cotton is oxide of tin, which is fixed by passing the goods through a solution of stannate of soda, and dipping them in very dilute sulphuric acid.

Starch has also a peculiar attraction for aniline colours, and may therefore be employed as a mordant. Reimann recommends to mix ¼ to ½ oz. of starch with 4 oz. of water, and to add this mixture to so much boiling water, that 1 lb. of cotton can be easily worked in it. The colour becomes faster and brighter if a hot solution of 60 grains of isinglass or gelatin be added.

*Spirit blue* is fixed on cotton by working it for twelve hours in a bath containing for each 5 lbs. of cotton 1 lb. of Castille soap, and dyeing in a bath to which some acetate of alumina has been added.

For dyeing with *iodine green*, the cotton is steeped over night in a cold solution of sumach, then passed through red liquor, and dyed in a cold aqueous solution of the colour.

*Saffranin.*—The cotton is well washed with soap,

and worked for two hours in a cold solution of acetate of alumina of 5° to 6° Tw., wrung out and worked in a strong soap bath of 60° C. After being washed, it is dyed in a solution of the colour at about 50° to 60° C. Thus yellowish pinks and cherry red may be produced.

*Phenylene Brown or Bismarck colour* is dyed on cotton by preparing the yarn with sumach and acetate of alumina, and working it in a cold or tepid dye bath. The addition of a little bichromate of potash produces darker and more reddish shades.

*Eosin* produces very delicate rose and pink shades. The cotton is first well worked in a hot bath containing 1 lb. of Castille soap for 10 lbs. of cotton, and is then steeped in a solution of 4 lbs. of sugar of lead. After these processes have been repeated two or three times, the cotton is worked in an aqueous solution of the colour, which goes on slowly but very uniformly.

*Quercitron, Flavin, and Fustic* are fixed by working the cotton, first in sumach, and then in a solution of tin crystals. For dyeing, either a solution of flavin, or a solution of the extract of the dyestuff, or a decoction of the latter, may be used.

A very good yellow is obtained by steeping the cotton in a decoction of 1 lb. of sumach, wringing out and working it for half an hour in acetate of alumina at 1° to 2° Tw. It is then again wrung out and dyed in a hot decoction of 5 lbs. of quercitron, to which 2 ozs. of tin crystals are added.

*Turkey Red.*—This beautiful colour, which is distinguished by its great brilliancy and stability, is produced by a very singular process. It is a madder colour, differing from all other colours produced by this root by being not only much brighter, but also by being less readily attacked by acids and by bleaching powder.

The methods which are used for producing this remarkable colour are more or less complicated, the first process, however, in all cases, being to saturate the cloth well with a vegetable oil. Generally *Gallipoli oil* is used; this is a common olive oil, containing extractive matters, and possessing the property of forming readily with a weak solution of pearl-ash or caustic soda a perfect emulsion, *i.e.*, a milky liquid, in which, by the naked eye, no oily drops can be seen. With this emulsion the goods are thoroughly saturated, and then exposed to the air for twenty-four hours in a room, which formerly was only heated in winter. The oiled cloth absorbs oxygen so rapidly that it becomes hot, and even sometimes takes fire. The higher the temperature gets during this oxidation, the more brilliant will be the colour; and therefore dyers prefer now to hang the oiled goods in a room having a temperature of 60° to 65° C., of course great care being taken to avoid combustion taking place. The same operation is repeated, according to the required shade, several times. It appears to be of advantage to add to the last bath some sheep's dung. The excess of oil, or rather that portion which has not been changed by oxidation or the action of the alkali, is now removed by washing.

The next process is *galling* and *aluming*, which is sometimes done by separate treatments. The cotton is passed through a bath containing sumach or nut-galls and aluminium acetate, then dried and aged, and now passed through chalk and water, in order to fix the alumina completely. The dyeing, which follows next, is done in a bath containing ground madder, garancin, or artificial alizarin. The cotton acquires now a heavy brown colour, which changes into a brilliant red by two or three soapings, or by a passage through an acid. Some dyers add to these baths pearl-ash or tin crystals.

Since the introduction of artificial alizarin the dyers prefer to treat the goods before soaping with caustic soda, to dissolve any excess of alizarin, which thus can be easily recovered, a process which would be more difficult in the presence of soap.

Turkey red consists chiefly of a peculiar compound of alizarin and fatty acids, which is soluble in ether and petroleum naphtha. On evaporating these solutions a splendid scarlet fatty mass is left behind, consisting of alizarin and fatty acids, which may be separated by dissolving in hot spirits of wine, and precipitating the fatty acids by the addition of a little water. The yarn or cloth, after being exhausted with the naphtha, loses all its brilliancy, and retains only a dull shade, resembling that which madder dyes on tin mordant.

The single threads of cotton dyed with turkey red contain the colour only on the surface, the oil preventing the alizarin from penetrating the fibre. This is undoubtedly the cause of the great brilliancy of this colour, because all colours appear much brighter when they are fixed on a white ground; while, if the whole colour is absorbed by the fibre, it appears dull. The presence of a fat is also undoubtedly the cause of the greater stability of turkey red, when compared with other madder reds. As the colour exists only at the surface, the quantity of alizarin required is but small, a piece of 60 yards taking up only about 5 to 6 ozs. of alizarin paste of 10 per cent., while to obtain a similar shade on cloth not oiled 2 lbs. would be necessary.

The quantity of alumina fixed in dyeing turkey red is always very small; some have even doubted that it plays a part in the process, while others believe that its presence is essential, the variations in shade being dependent on the quantity of the alumina, and not of that of the oil.

The following facts will show why this point is not easy to settle.

An imitation of turkey red is now obtained by impregnating the cloth with red liquor, drying, and passing it through a soap solution, in order to obtain a compound of alumina with fatty acids. The cloth thus prepared assumes on dyeing with madder or alizarin a very bright red. In this process a piece of 60 yards requires only about $\frac{3}{4}$ gals. of red liquor at 7 Tw., containing 200 grains of alumina; but of this quantity only a fraction is fixed. This is shown by the fact that when alizarin is fixed by steaming, the same shade requires only about $\frac{1}{6}$ of that quantity of alumina, and this is also only partially fixed,

most probably not more than one-half of it remaining in combination with the alizarin. From these numbers, and the quantity of alizarin which is fixed in dyeing, we come to the conclusion that a piece 1 yard long and $2\frac{3}{4}$ feet wide contains about $\frac{1}{60}$ grain of alumina and $\frac{1}{200}$ of pure alizarin, while the ash of the piece weighs about $\frac{1}{6}$ of a grain.

A very good imitation of turkey red is also produced by dyeing goods, mordanted with a strong solution of acetate of alumina, with anthrapurpurin.

*Brazil wood*, and the other red woods, are used for dyeing common reds. The goods are mordanted by steeping them in hot sumach liquor, and then passing them through red spirits (stannic chloride). After washing, they are dyed in a bath containing brazil wood and some fustic or quercitron. The latter are added in order that the yellow which they impart may brighten the crimson, produced by the red woods, into a scarlet.

Inferior reds are obtained by simply saturating cotton with a solution of Brazil wood extract in tin spirits and passing through water; or they may be obtained by first fixing an alumina mordant and then dyeing.

Examples.—*Common Red*:—Steep in a hot decoction of sumach and allow to cool, wring, and pass in tin spirits at 2° Tw. Wash, and pass for half an hour in a hot decoction of 3 lbs. of Lima wood and 1 lb. of fustic.

*Crimson.*—3 lbs. of sumach.
Tin spirits, at 20° Tw.
3 lbs. Brazil wood.
1 lb. logwood.

Proceed as above.

*Logwood* is chiefly used for dyeing cheap blacks; it yields with alumina alone a purplish black, and with iron mordant a dull brownish black. A mixture of the two is therefore generally used, and to the dye bath quercitron and other dye woods are often added to modify the shade.

Faster blacks are obtained by using with the logwood some astringent matter. The goods are first steeped into a decoction of sumach or nut galls, then passed successively through lime water, solution of copper sulphate, boiling logwood liquor, and lastly through a solution of green vitriol.

A fine black may also be obtained by first fixing an iron mordant, and then steeping in a bath containing sumach and logwood.

The old fast black was obtained by first dyeing with indigo, then passing the goods through a decoction of nut galls or sumach, and finally through a solution of green vitriol.

Colours Fixed by Oxidation.—The colours of this group are the same as those employed in printing. It is, therefore, not necessary to repeat what already has been said about the formation of these colours; it is sufficient to describe simply the process.

*Catechu* is much used for dyeing brown or fawn; the goods are worked in catechu liquor containing a copper salt, and then in a weak solution of potassium dichromate. Other shades are obtained by steeping the goods, which have been worked in the catechu bath, in weak caustic soda or milk of lime, and then exposing them to the air.

*Aniline black* can be dyed by different methods.

According to Persoz, a good black is obtained by steeping cotton in a solution containing 8 per cent. of potassium dichromate, and then working it in a solution consisting of 10 parts of aniline, 10 of sulphuric acid, 25 of strong hydrochloric acid, and 200 of water. The yarn is dried on hot plates and steamed.

Müller-Pack uses ferrous chloride, which he prepares by dissolving 3 parts of iron in a mixture of 10 parts of hydrochloric acid and 10 of water; this solution is diluted with so much water that it stands at 70° Tw. The yarn is steeped in this liquor for two hours, and then exposed to the air for twelve hours. On the other hand, a solution is prepared by dissolving 3 parts of aniline and 5 parts of hydrochloric acid in water, and adding to this liquid a solution of $2\frac{1}{6}$ parts of potassium chlorate in 30 parts of water.

The yarn is steeped in this mixture and then heated gradually from 30° to 50° C. in a closed vessel; then after being exposed to the air for some time, it is passed through a solution of potassium dichromate. The black thus produced assumes a bluish shade by passing the goods through dilute sulphuric acid and washing them with water and dilute caustic soda. Lucas' soluble aniline black, which has been described under printing, is also used for dyeing. Another soluble black is prepared by Coupier; he heats a mixture of 175 parts of commercial aniline with an equal quantity of nitrobenzol, 200 parts of hydrochloric acid, 16 parts of iron filings, and 2 parts of finely divided copper, for eight hours gradually to 200°. The black mass thus obtained is soluble in dilute acids, and is readily fixed upon the cotton after passing through this solution, by dipping it in an alkaline bath.

Another method for producing an aniline black has been proposed by Lauth. He dyes the cotton first with manganese brown, by working it for an hour in a bath of manganese chloride at 70° Tw., and then steeping without washing in boiling caustic soda at 17°, in which some lime is suspended. After washing it is passed through a tepid solution of bleaching powder. The yarn thus charged with bistre is again washed and steeped in a cold acid solution of aniline for one or two minutes. According to the shade which is wanted, the aniline solution is composed of 10 to 20 parts of aniline, 60 of sulphuric acid, and water to make up 1000 parts. After dyeing, the cotton is washed and passed through a boiling solution of soap or soda crystals.

*Indigo.*—Among the colours fixed by oxidation indigo is the most important. The process which is used for dyeing cotton with indigo has already been shortly explained (see *Resist Style*).

Finely ground indigo is very thoroughly mixed with hot milk of lime and placed in a vat, into which a hot solution of ferrous sulphate is afterwards gradually introduced. By the reaction thus set up indigo white is formed in the presence of an excess of lime, and quickly dissolves. The proportions which are generally used are—

| | |
|---|---|
| Indigo, | 1 |
| Crystallized ferrous sulphate, | 3 |
| Slacked lime, | 3 |

But some dyers prefer an excess of lime, although the proportions as given above contain already more lime and sulphate than required by the theory. This, however, is necessary; for the surface of the liquid being exposed to the air, a scum of regenerated indigo is always floating on the surface; which on gradually sinking down, redissolves again.

The lime cannot be replaced by other alkalies, because vats prepared with caustic soda oxidize much more rapidly than lime vats; the reason being that the insoluble lime protects the ferrous hydrate and prevents its rapid oxidation. Moreover, the compound of lime and indigo white is much more easily absorbed by cotton than the soda compound. After mixing the components, the liquid is left to stand for some hours.

The cotton is now immersed in the vat until saturated with the liquid, and then the colour developed by exposing the goods to the air.

By varying the strength of the vat as well as the number of immersions, different shades, ranging from pale blue to bluish-black, can be obtained.

In order to obtain uniform and stable shades it is best to commence with a weak vat, and then use gradually stronger ones. The indigo is thus made to penetrate the fibre more completely.

Mineral colours are also much employed for the dyeing of cotton. It is not necessary to explain here the methods which are used, because they are exactly the same as those employed in chemical printing; the principle being to deposit, by means of a double chemical decomposition, a coloured precipitate in the fibre.

It can further be easily understood, that by uniting several of the colours which have been described on the same fibre, any desired shade can be produced. The following examples may serve for illustrating this point:—

*Green colours* are produced by first dyeing a light indigo blue in the vat, and after fixing an alumina mordant, dyeing in quercitron or fustic liquor. Or the blue goods may be changed into green by using a lead mordant, and then raising the colour in potassium dichromate.

Good greens are also obtained by dyeing with quercitron or fustic on Prussian blue.

*Grey colours* are in most cases nothing but dilute blacks, and therefore the same materials which are employed for producing black are used, only in smaller quantity. The tints are modified into yellowish, bluish, reddish grey, &c., by the addition of quercitron, fustic, Brazil wood, logwood, catechu, &c.

*Brown colours* are generally obtained by a mixture of yellow, red, and blue. Thus, quercitron may be dyed on a tin mordant, fixed by sumach, and the colour be raised by means of Brazil wood and logwood. Or the cotton is first dyed with annotta, then worked in a decoction of sumach and fustic, passed through an iron mordant, and the colour raised in a decoction of logwood and Brazil wood.

The Dyeing of Wool and Silk.—All substantive colours dye wool and silk without the intervention of a mordant; but in several cases mordants are used, because it has been found that the colours thus obtained are brighter and faster.

Adjective colours always require a mordant, which may be applied in two different ways:—

(1) The mordant is first fixed on the wool or silk, which are then worked in a solution of the dye stuff.

(2) The wool or silk is dyed in a bath containing the colouring matter and mordant in solution together. The chemical process taking place in this case may be illustrated by the following example, which also serves to show the different affinity of wool and cotton for colouring matters:—

Dissolve a few grains of flavin in boiling water, and add some drops of a solution of stannous chloride (tin spirits). A yellow precipitate will be formed, consisting of a compound of flavin and tin oxide. Add now a little oxalic acid or tartaric acid; the precipitate will completely dissolve, and a colourless solution will be obtained. Immerse then in the boiling solution some wool and some cotton; the wool will very soon assume a bright yellow shade, while the cotton will remain perfectly white.

We thus see that organic acids have the property of dissolving the compound of flavin and stannous oxide; but wool has the power to take it up from such a solution, and of combining permanently with it, while cotton does not possess this property.

The mordants used in the dyeing of wool and silk are the same as those employed in the printing and dyeing of calico. But there is one specific mordant for wool which must be mentioned here. This is potassium dichromate (bichromate of potash), which has the property of combining with wool, which takes it up from an acid solution, probably partially, in the form of chromic oxide. Potassium dichromate is used chiefly as a mordant for browns, olives, greys, and blacks; and produces very full colours, evidently on account of its oxidizing properties.

*Preparation of Wool for Dyeing.*—The first process to which spun wool is subjected is to remove all the oil with which the wool becomes saturated in spinning. This is effected by washing it in a warm bath (not exceeding 50° C.) containing a solution of soap and ammonia, or soda crystals, or soap only. After being well washed, the wool is thoroughly washed in running water, and is then ready for dyeing.

*Preparation of Silk for Dyeing.*—Raw silk is prepared for dyeing by *scouring* it, or passing it through a hot soap solution, which removes the gummy matters. After washing, it is bleached by gaseous sulphurous acid, then passed through a hot solution of tartar, and finally well washed with warm water.

Silk has not the same attraction for colours as wool has. Some of them go much more readily on the former, others more easily on the latter; the methods used for dyeing these fibres are therefore not always the same, but in most cases similar enough to allow us to consider them together. Many methods employed for dyeing wool cannot be used for silk at all,

because it does not stand such rough treatment as wool, being a much more delicate material.

*Aniline Colours.*—The salts of rosaniline, as well as those of the different methyl and ethyl violets (Hofmann's & Paris violets) are mostly soluble in water, and the dyeing of them on wool is a very easy operation; the yarn is simply suspended in a hot and not too concentrated solution of the colour, until it has assumed the required shade.

It is very important that the colour should be completely in solution, as undissolved particles would attach themselves to the fabric and produce spots. A very good plan is to mix the colour with glycerin by grinding, boiling the mixture with water, and filtering through woollen cloth. Another simple method which some dyers use is the following:—A woollen filter is placed in one corner of the dye beck, so that its bottom dips some inches under the liquid. In the filter the required quantity of colouring matter is placed, tied up in a bag of flannel; the colour then dissolves only slowly, and being filtered through two layers of wool, the solution is free from any undissolved particles and impurities.

In dyeing wool the solution is usually hotter than that used for silk. To produce even shades the solution of the colour is only gradually added, and before each addition the fabric must be taken out, and only put back after the bath has been well stirred up.

The phenyl violets and blues (spirit blue) are almost insoluble in water, but readily soluble in alcohol and wood spirit. To dye with them an alcoholic solution, generally mixed with glycerin, is added gradually to hot water, in which the wool is suspended. The addition of glycerin has been found of advantage, because it increases the solubility of the colour, which, moreover, by the evaporation of the alcohol would be precipitated on the wool too rapidly and unequally. By adding to the bath stannic chloride and tartar or bisulphate of soda, the brightness of this colour is much increased.

Silk is best dyed in a soap bath, and the colour brightened by a passage through dilute sulphuric acid.

*Alkali Blues* are best fixed on silk and wool by adding to a hot solution of the colour a little borax or soda crystals. The wool takes up the salts in an almost colourless state, but fixes them completely; when it has taken up sufficient, which is easily seen by dipping a little of it in acidulated water, the whole is washed with water, and the colour raised in a bath of very dilute sulphuric acid.

The soluble blues may also be dyed on wool by the following process:—

10 lbs. of wool are boiled for half an hour or more in a bath containing ¾ lbs. of tartar, ½ lb. of aluminium sulphate, 5 oz. of solid stannic chloride, and ½ to 1 lb. of sulphuric acid at 150° Tw., and then dyed in a boiling solution of the blue, to which some sulphuric acid has been added.

*Iodine Green.*—Wool is dyed by two methods:—

1. It is prepared in a bath containing 3 lbs. of hyposulphite of soda and 1½ lb. of hydrochloric acid; and being heated to 50° C., the temperature is gradually raised to 70° C., and then the wool is washed with cold water.

To the dye-bath some acetic acid is added, and the dyeing commenced at 50° C., and the temperature gradually raised to 70° C.

2. Two baths are prepared, one containing the colour and some ammonia, in which the wool is slowly boiled until it assumes a greyish-green shade, which is brightened in the second bath containing acetic acid, and heated to 40° C.

Silk will dye in a warm aqueous solution, to which some picric acid is added if a yellowish shade be required. It may also be dyed in a soap bath, and the colour brightened in a bath containing acetic acid, and if necessary, some picric acid.

*Saffranin*, which produces a beautiful pink and rose, is simply dyed in a dilute aqueous solution, both on wool and silk.

*Magdala red* produces a similar shade, but the colour exhibits a beautiful fluorescence.

*Manchester brown* is dissolved in hot water, to which for one part of the colour half a part of sulphuric acid is added.

*Picric acid* fixes very easily on wool and on silk in an aqueous solution. To obtain brighter and faster shades wool is previously mordanted with alum and cream of tartar, while a fast yellow on silk will be obtained by passing it after dyeing through a warm solution of sugar of lead, and brightening the colour in a weak soap solution.

*Naphthalene yellow* dyes a very pure yellow, not showing the greenish tinge which is imparted by picric acid. It is therefore also much employed for dyeing orange or scarlet on silk and wool. To a boiling dilute solution of the colour the required quantity of pure mageuta is added, the proportions varying according to shade—a good scarlet being obtained by using 30 parts of the yellow to 1 part of magenta.

*Eosin* dyes on wool and silk, pink, rose showing a beautiful scarlet reflection, and very bright but yellowish scarlets. It is fixed on wool by dyeing in a boiling aqueous solution, containing a little acetic acid, and raising the colour in a boiling solution, containing for 100 parts of wool 2 parts of oxalic acid, and 2 parts of acetate of alumina.

Silk is first softened in boiling water and dyed in a soap solution, which, for the lighter shades, is acidulated with acetic acid, and for deeper ones with sulphuric acid.

*Aurin* or *yellow corallin* produces on wool a bright and fast orange. It is almost insoluble in water, but dissolves readily in dilute alkalies; but is not taken up by wool from such a solution. Therefore, to dye with it, acetic (or some other acid) is carefully added to a boiling alkaline solution of the colour, until the liquid begins to become turbid. The alkali is now completely neutralized, and the colour quickly absorbed by the wool. Another good method is to add first an alcoholic solution of aurin to boiling soap-water, and then an acid, until the liquid becomes turbid. This bath is also used for silk.

*Peonine* or *Red aurin* is dyed in the same way, and produces a fine scarlet.

*Purree* yields different yellow and orange shades, and may be used for silk and wool. To obtain the darker shades the colouring matter is dissolved in the smallest quantity of nitric acid, and the solution diluted with water. Yellow shades are obtained by dissolving purree in a solution of borax and sal-ammoniac.

*Annotta* is also much used for dyeing orange tints, chiefly on silk, which is simply worked in a warm solution of the dyestuff and soda crystals, to which sometimes some soap is added. After washing in warm water, the colour may be brightened by passing the silk through a dilute solution of tartaric acid.

*Safflower* is fixed on wool and silk in the same way as on cotton. The only precaution which has to be taken is to employ a safflower precipitate which is completely freed from the yellow colouring matter, or else the latter would also fix on the animal fibre, and spoil the pure rose-tint.

*Archil* and *French purple* were, before the discovery of the aniline colours, much used for dyeing different shades of purple, violet, lilac, lavender, &c. By employing an acid at the same time the redder shades are obtained, while, in presence of an alkali, the shades become bluer.

*Indigo.*—This is one of the most important colours for woollen goods, being very fast and stable, and not affected by alkalies nor by most acids. There are two methods for fixing indigo on wool :—

(1) *Indigo Vat, or Hot Vat.*—This style of dyeing is very similar to the dyeing of cotton by indigo, the wool being immersed first in an alkaline solution of indigo white, and then exposing it to the air. But the preparation of the vat is quite different; none or only little lime being used, nor any ferrous sulphate, the constituents of the vat being the carbonates of potassium or sodium, or the caustic alkalies, and some organic matter, which readily undergoes a peculiar kind of fermentation, by which hydrogen is evolved. This combines with the indigo blue and forms indigo white, which dissolves in the alkali. The different kinds of vats which are used are the following, which are all worked hot :—

(*a*) *Woad and Pastel Vat.*—Formerly the only indigo-yielding constituent of this kind of vat was woad, but now finely-ground indigo is always added. The colouring matter of woad undoubtedly adds to the effect, but its principal use is in furnishing the fermentable matters. Pastel is a kind of woad growing in France; it is richer in indigo blue than common woad, but is also now only used in combination with indigo. To prepare a woad vat, water is heated to the boiling point, and 50 parts of woad, 3 of madder, 3 of bran, and 9 of pearl-ash are introduced, and then 3 parts of indigo. The mixture assumes, after standing for eight to ten hours, a greenish-yellow colour, and changes into a brown by the addition of 4 to 5 parts of slacked lime.

(*b*) *Indian or Potash vat* is prepared by using equal parts of indigo, bran, and madder, and three times as much pearl-ash, and heating the mixture with water to 50° C. The addition of madder to these vats is believed to produce darker colours, having a violet tint. This, however, appears to be merely fancy, because it is very improbable that under these conditions the colouring matter of madder could be fixed on the wool. The utility of madder is undoubtedly due to the sugar and other fermentable bodies which it contains.

(*c*) *German Vat.*—This is prepared by heating water to 50° to 60° C., and adding first soda crystals, bran and indigo, and then, when the fermentation has well set in, some lime. To quicken the fermentation molasses is often added, and lately it has been proposed to substitute the bran by ground turnips or other similar roots, or fleshy fruit.

The dyeing in these vats is very simple: the goods after being well wetted are suspended in the liquor for one or two hours, and well agitated all the time to insure a uniform colour. On taking them out they rapidly colour blue, and if the required shade has not been obtained the goods are again repeatedly immersed. They are then washed, first in dilute acid, and next with running water.

The colours dyed by the vat are very fast, but dull, and are chiefly applied to knitting wool and the cloth used in the army and navy.

(2) *Dyeing with Indigo-sulphuric Acid.*—The blue thus obtained is brighter, but less stable, than the vat blue. It has now been almost completely superseded by aniline blue. Formerly each dyer prepared his own indigo solution by dissolving 1 part of indigo in 4 to 5 parts of Nordhausen acid, and dyeing from this solution after diluting it with water. The shades thus obtained are not pure and bright, because indigo contains also reddish and brown colouring matters, which readily fix on wool. To avoid that, wool is boiled with the solution of indigo-sulphuric acid until it is saturated and assumes a deep bluish-black colour. It is now washed and boiled with a weak solution of soda crystals (3 parts to 1000 parts of indigo). The pure blue colour now dissolves again, while the wool retains the dirty reddish and brown colours. The blue solution thus obtained dyes, after being acidulated, much purer shades than a solution of indigo in sulphuric acid.

These two preparations of indigo are now replaced by indigo carmine (the sodium salt of indigo-sulphuric acid). The wool is first boiled in a solution of alum and tartar, and then dyed with an acidulated solution of the carmine. The blue thus produced is chiefly used for producing a brilliant green with picric acid, which is simply added to the dye-bath as soon as the wool has taken up a quantity of the blue. Silk is dyed with indigo in the same way.

To obtain a bright green the dyeing must not be done in tin, but in copper. To dye 10 lbs. of wool with picric green, the water is first boiled with 1 or 2 lbs. of aluminium sulphate; then 1 lb. of crystallized alum and 1 lb. tartar is added. It is now dyed with indigo carmine, and as soon as the blue has gone on the wool, a sufficient quantity of picric acid is added to the bath. A good imitation of French purple is obtained in the following way :—

50 lbs. of yarn are boiled in a tinned vessel with 8 lbs. of alum, 2½ of tartar, and 5 of tin solution. The wool is removed, some cold water is added, and a sufficient quantity of indigo carmine; the wool is dyed in this solution at a boiling heat, and left over night. It is now washed and dyed at 75° C. in a bath containing 10 lbs. of violet mordant, and a sufficient quantity of magenta crystals.

The tin solution is prepared by dissolving 12 lbs. of granulated tin in a mixture of 60 hydrochloric acid and 9 nitric acid.

The violet mordant is obtained by dissolving 16 lbs. of potassium dichromate, and adding a mixture of 32 lbs. of sulphuric acid at 130° Tw., and 32 lbs. of water, and then very gradually 12 lbs. of methylated or wood spirits. The solution thus obtained contains chrome alum; and it appears therefore much more rational to use this salt, which is now prepared, or rather obtained as a bye-product, in the manufacture of artificial alizarin.

*Red Indigo Carmine, Indigo Purple*, is the sodium salt of indigo-purpuric acid (see Indigo). It dyes a deep violet, and is chiefly used for modifying the shades produced by archil and French purple.

*Cochineal* is a most important material for dyeing wool, producing a splendid bright, pure, and fast scarlet. It is also employed for dyeing orange, pink, rose, purple, &c.

Scarlet is obtained by boiling the wool with ground cochineal, stannous chloride, and cream of tartar or oxalic acid.

To produce a bright scarlet, the water must be first purified. This is done by heating it to 75° to 90° C., and then adding ½ to 1 lb. of perchloride of tin. Soon a yellowish-grey thick scum appears at the surface, which is removed; the water must all the time be kept near the boiling point, but must not boil. After it is perfectly clear, for each 10 lbs. of wool, 1 lb. cream of tartar, 1¼ lbs. solid chloride of tin, and 1 to 2 lbs. ground cochineal are added, and the wool left in the hot solution for half to three-quarters of an hour.

In the place of cream of tartar oxalic acid may be used; but in this case the water must not contain lime salts, or if so, they must be carefully removed, or else oxalate of lime is precipitated on the wool, and the colour becomes dull.

*Lac Dye* is employed in a similar way: for 10 lbs. of wool are required, according to shade, 1 to 2 lbs. of cochineal; 1 lb. of chloride of tin solution; ½ lb. of tartar; and 3 to 6 lbs. of a mixture of equal parts of lac dye and hydrochloric acid, which is kept ready for use.

This scarlet is not so bright as cochineal scarlet, and has a yellow tinge, but is much used because it it is a very fast colour, which is not much altered by fulling.

The tin solution is prepared by dissolving 5 parts of solid perchloride of tin, and 1 part of tin crystals in so much water that it stands at 34° Tw.

Yellowish scarlets are obtained by adding to the dye beck a decoction of fustic, while by the addition of red woods, archil or logwood, darker or brownish shades are produced.

*Cochineal Rose and Pink* are dyed with ammoniacal cochineal; the mordants being alum, stannous chloride, and cream of tartar.

In order to obtain bright cochineal pinks, the yarn is first treated with a cold solution of 1 lb. of soda crystals in 10 lbs. of water, and then very well washed. It is mordanted in a tinned boiler in a solution of—

1 lb. of alum.
½ lb. of tartar.
1 lb. of tin solution.

and dyed in a hot, but not boiling solution of ammoniacal cochineal, to which some tin solution has been added.

To obtain a scarlet on silk, it is first dyed orange with annotta, and then dyed with ammoniacal cochineal.

In dyeing with cochineal, as well as with other colours, a most important point is to stir the dye-bath well up after the dyestuff has been introduced. If the dyed wool appears spotted or streaky, it is in ninety cases out of a hundred the fault of the dyer, who has not paid the required attention to this point, and was in too great a hurry to commence dyeing before the dye bath had been thoroughly mixed.

*Brazil wood* and the other red woods are used for obtaining a bright but not a fast scarlet. For this purpose the wool is first mordanted in a boiling solution of alum (which must be free from iron), cream of tartar, stannic chloride, and copper sulphate, for one or two hours. After washing, the yarn is left lying for two or three days, and then dyed in a boiling decoction of Brazil wood, to which, according to shade, some logwood may be added.

The following recipe yields a very bright red:—

Fill a copper boiler with water, and add to the boiling liquid—

4½ lbs. of pure alum.
6 oz. of tartar.
1¼ oz. of blue vitriol.
6 oz. of tin solution.

Boil for eight minutes, add a little cold water, and boil the yarn for one and a half hours, and allow it to remain in the liquid for two or three days. Wash and dye for two hours in a boiling decoction of Lima wood.

In the place of tartar cheaper substances are often used, principally acid sodium sulphate (bisulphate of soda).

A faster colour produced by Brazil wood is *chrome brown*, which is obtained by first mordanting the wool in a boiling solution of potassium dichromate and tartar or sulphuric acid, and after leaving it hanging in the air for some hours, washing it quickly with a little water. The yarn is then dyed in a boiling solution of Brazil wood, to which, according to the shade required, either fustic or logwood is added.

Cheap reds on silk are obtained by passing the goods first through a solution of extract of Brazil wood, then airing them and passing them again through the bath, to which a solution of stannic chloride has been added. Different shades are produced by the addition of logwood or fustic.

*Logwood* is chiefly used for dyeing greys and blacks. Formerly these colours were produced by means of

salts of iron, but now *chrome black* is almost exclusively used for wool. The yarn is either first boiled with logwood and then passed into a hot solution of potassium dichromate, or the wool is first mordanted with chrome, and then dyed in a decoction of logwood and fustic.

A good black is obtained by boiling wool for an hour and a half in a solution containing 5 parts of potassium dichromate, 2 parts of copper sulphate, and 1 part of sulphuric acid, and leaving it over night in the bath. The dye bath consists of a decoction of 100 parts of logwood, 10 parts of fustic, and 11 of ammonia.

Logwood is also used for giving a violet shade to goods dyed in the indigo vat, the mordant being a tin salt.

Logwood black on silk is obtained by mordanting with ferric nitrate, and then dyeing in logwood liquor, to which fustic is added if a brownish black be wished for. Very often an indigo-blue ground is first dyed on the silk.

*Fustic* and *quercitron* were, before the artificial colours were known, the only yellow dyestuffs of importance which were used for the dyeing of wool and silk. They are fixed in a way very similar to that in use for cochineal; quercitron requiring the same mordants, while for fustic alum is used, generally with the addition of sulphuric acid, which prevents the colour going on the fibre too rapidly. This is essential for deeper shades, which else would become dull and patchy.

Fustic was, before the use of picric acid, generally employed for dyeing green on an indigo-blue ground. It is also employed, as well as quercitron, for shading the colours produced by red woods, logwood and archil, and chiefly for the latter, with which it gives different bronze and olive shades.

The following proportions produce a bright and full yellow on 10 lbs. of wool:—Clear the water by boiling it with 4 ozs. of aluminium sulphate, then introduce 4 lbs. of quercitron, tied up in a bag, and 3 pieces of glue; boil one hour with the wool, remove the bag and add ½ lb. of aluminium sulphate, ½ lb. of tartar, and 1 lb. of tin chloride, which is prepared as follows:—To 55 lbs. of a solution of perchloride of tin at 110° to 115° Tw., add 5 lbs of tin crystals, and so much water that it stands at 38° Tw.

Orange tints are produced by adding cochineal.

*Turmeric* and *weld* serve principally for shading green and olive colours, while *annotta* is used in conjunction with fustic, red wood, cochineal, aniline red, &c., for different shades of yellow and orange.

*Catechu-brown* is produced on wool by passing it through a boiling decoction of catechu for some time, then adding to the bath a copper salt or potassium dichromate, and working the wool in it until it has acquired the proper shade.

*Tannin-black* on wool is obtained by using an iron salt as mordant, and then dyeing in a decoction of nut-galls, sumach, or any other astringent. The so-called *Sedan-black* is produced by imparting to the wool, first, a blue ground by the indigo vat, and then boiling it with sumach and logwood. It is then aired and brought back into the bath, to which some ferrous sulphate has been added. These operations must be repeated until the desired black is obtained. Sometimes copper sulphate is added to the bath, while, if a more brownish-black be desired, fustic is also used.

To obtain a good black on silk it is first galled in an infusion of nut-galls or sumach, and then worked in iron liquor. The silk thus treated becomes hard and rough; it is therefore worked in an emulsion, obtained by mixing caustic soda and oil, or in a soap solution.

A good black is also produced by mordanting with ferric nitrate, and passing successively through sumach liquor and soap solution. By repeating the mordanting and soaping, a very large quantity of ferric oxide is fixed by the silk. This is called *weighting*, and is necessary for good black silk, which without a certain amount of mineral matter would not possess that crispness which is required. However, the weighting of silk is often carried on too far, and becomes an adulteration. There is found black silk in the market leaving on incineration an ash amounting to 80 per cent. and more of the original weight. But it is not only black silk which is thus charged with mineral matters; the weighting is also carried out in the dyeing of other colours by charging the silk with stannic oxide, of which it can be made to take up a very large quantity by immersing it in a solution of stannic chloride, and keeping the liquid neutral.

A cheap black may be produced by mordanting silk twice with iron nitrate, and dyeing it in a decoction of logwood, to which some quercitron and blue vitriol has been added. The silk is then washed, and passed first through a solution of soap and then through a solution of basic acetate of lead. Thus the silk becomes weighted with a compound of lead with the fatty acids of the soap, and on exposing this to sulphuretted hydrogen black lead sulphide is formed.

Aniline black is also employed for the dyeing of silk and wool.

*Prussian blue* is generally fixed on wool by dissolving yellow prussiate of potash in water, adding one-fourth of sulphuric acid, and passing the wool into the solution, which is gradually heated from 60° to 90° C. The wool, which has now a bluish-green colour, is then passed through hot dilute sulphuric acid, to which some stannous chloride has been added to give a purple tinge to the blue. Since the introduction of aniline blue, Prussian blue is not much used for dyeing wool; not only because the former is a much more stable colour, but also because the dyeing of Prussian blue is a dangerous operation, on account of the prussic acid set free, which often overpowered the workmen if they did not take sufficient care.

The peculiar shade of Prussian blue is well imitated by the following process:—

10 lbs. of yarn are boiled for half an hour in a tinned vessel with ¾ lb. of alum, 1½ of tartar, and ½ lb of sulphuric

acid, at 130° Tw., and sufficient water. Then indigo carmine and a sufficient quantity of aniline violet is added.

Prussian blue on silk is obtained by mordanting it in ferric nitrate, to which sometimes stannic chloride is added, and working it in a solution of yellow prussiate. It is then washed and passed through dilute sulphuric acid.

After having discussed the principles on which the dyeing of wool and silk depends, the printing of woollen goods deserves a short notice.

*The Printing of Wool.*—Well washed and bleached wool always possesses a faint yellowish tint; but as in printed goods, bright colours appear only in all their purity if they are in contrast with a perfectly white ground, the first preparation which wool for printing has to undergo is to *dye* it *white*. This is done by passing it through a warm solution of soap, to which a little indigo carmine has been added. Thus the yellow and blue, being complementary colours, neutralize each other; and by varying the quantity of indigo carmine, greenish or bluish whites may be obtained. The wool is now placed in the sulphur chamber, and then passed through a warm solution of soda-ash. The next operation is *alumingy*, or working the wool in a tepid solution of alum. The colours produced on wool by printing are all steam colours. The steaming is not only required for fixing the colours, but also to obtain pure and bright shades. Without steaming the colours are dull and unsightly.

The following examples will be sufficient for illustrating the methods which are used in the printing of wool:—

(*a*) *Aniline colours* are simply printed by using a thickened aqueous solution of the colour, and steaming the printed goods.

(*b*) *Logwood black* is produced by using a solution of the extract, to which is added copper sulphate or potassium chromate as oxidizing agent, alum and ferric nitrate as mordants, and oxalic acid to keep the combination of mordant and colour in solution, and thus enable it to penetrate the wool.

(*c*) *Cochineal reds* of varying shades are obtained by using either a decoction of cochineal or ammoniacal cochineal, to which stannic chloride and tartaric or oxalic acid are added.

(*d*) *Green* is obtained by using indigo carmine and extract of fustic, quercitron, or berries, together with alum, chloride of tin, and tartaric or oxalic acid. Fustic is generally used instead of quercitron, because it is cheaper, and the advantages which the latter has in dyeing are not so conspicuous in printing. Sometimes a little cochineal is added, to correct the greyness of the indigo blue.

(*e*) *Yellow* and *red Aurin* yield orange and red shades, which may be produced in different ways. Thus, on adding chloride of zinc to an alkaline solution of aurin, an orange lake is precipitated, which is fixed by mixing it with oxalic acid and gum, and steaming the goods after printing. Or aurin is mixed with calcined magnesia, water, and a little glycerin, and the colour fixed by steaming. Thus a fine red, a compound of magnesia and aurin, is obtained.

*The Printing of Delaines.*—Delaine is a mixed fabric, of which the warp is cotton and the weft wool. As these two materials possess such a different attraction for colours, great experience is required to obtain the two threads of the same shade. The colorist must be able to produce colour mixtures in which the colours do not interfere with each other, and which deposit uniformly both on the animal and the vegetable fibre. Cotton is best mordanted and dyed in neutral liquids, and at a moderate temperature; while on wool the colour fixes better at a high temperature, and in the presence of a little free acid. To equalize the attraction of the fibres as much as possible, they are always first impregnated with oxide of tin. Frequently the delaine colours are composed of two, one capable of fixing itself on the wool, and the other on the cotton.

A good example of such a colour is a mixture of steam Prussian blue for the cotton, and indigo carmine for the wool.

When delaine colours are unskilfully mixed, the two threads assume different shades, and threadiness is thus produced.

*The Testing of Colours on Dyed and Printed Fabrics.*—The detection of organic colours on dyed or printed goods is in some cases very easy, and in others very difficult. If only simple colours are present, a few tests are generally sufficient to determine the nature of the colour; but when the colour is a mixture of two or more bodies, it requires great practice to detect them.

In the following we give only those tests by which the more important colours may be distinguished from each other.

(1) Red Colours.

*Rosaniline* or *Aniline red* changes into yellow by moistening it with dilute hydrochloric acid, and becomes red again by washing with water. Dilute caustic soda bleaches it very slowly, and ammonium sulphide more quickly. Acetic acid restores the colour.

*Saffranin* becomes blue by treating it with strong hydrochloric acid: washing with water restores the colour. It is not changed by dilute caustic soda, and may thus be readily distinguished from *safflower*, which alkalies change into yellow, while dilute acids restore the colour.

Saffranin may also be detected by extracting it with alcohol, evaporating the solution to dryness, and treating the residue with sulphuric acid and water, as described under *Saffranin*.

*Turkey red* is readily recognized by its brilliant shade, and is distinguished from all other red colours by not being changed by dipping it for a few moments into a very dilute boiling solution of bleaching powder, by which all other reds are discharged. It is also not altered by dilute hydrochloric acid. By exhausting the tissue with ether, and evaporating the solution, a brilliant scarlet fat is left behind; and this, when boiled with strong caustic soda, yields a purplish-blue solution, from which acids precipitate alizarin in orange flakes. The fabric, after being treated with ether, exhibits a dull cherry-red colour.

*Madder Red and Pink* leave on incineration an ash which is rich in alumina. The colour is not discharged by boiling with soap and water. On treating the colour with dilute hydrochloric acid it becomes yellow, and after washing dilute caustic soda dissolves it with a purplish-blue colour. If this solution be not too dilute, pure alizarin may be obtained from it by adding dilute hydrochloric acid, and collecting the precipitate on a filter. The washed residue dissolves readily in alcohol, and on adding a solution of copper acetate a purple precipitate is obtained.

*Brazil Wood*, &c.—Tissues dyed by it or other red woods leave an ash containing alumina or tin oxide. A boiling soap solution changes the colour into yellow. By treating the colour, first with hydrochloric acid, and then with milk of lime, and passing through a solution of soap, a violet is produced, which soon disappears again. Concentrated sulphuric acid changes the colour into a bright cherry red, and dilute sulphuric into a bright orange; on boiling with a solution of aluminium sulphate, the liquid colours orange.

*Cochineal red* leaves also an ash containing tin oxide or alumina. Dilute caustic soda changes it into purple, and concentrated and dilute sulphuric acid into yellow. Boiling soap solution discharges the colour. On boiling with aluminium sulphate, a bluish-red solution is obtained.

*Ammoniacal cochineal* is not changed by dilute sulphuric acid.

Purple and Violet Colours.

*Hofmann's and Paris Violets* are only slowly changed by alkalies; and if the colour be more or less discharged, it is restored by acetic acid. Dilute hydrochloric acid turns it yellow, but on washing with water the colour appears again.

*Phenyl violets* are not changed by dilute hydrochloric acid, but quickly discharged by dilute caustic soda; dilute hydrochloric acid restores the colour.

*Manve* is not changed by dilute soda, and is turned into blue by strong hydrochloric acid.

*Archil or French purple* assumes a bluish tint, by treating it with dilute alkalies. Dilute acids change the blue into a red; ferric chloride weakens the colour, and gives it a yellowish tinge.

*Madder purple and lilac* leave an ash containing ferric oxide. The other tests are the same as for madder red.

*Logwood blue or violet* leaves an ash containing alumina. Dilute hydrochloric acid changes it into yellow or red, which by the action of aluminate of soda becomes blue again. On boiling with milk of lime, and then with soap, the colour is discharged. In boiling aluminium sulphate, it dissolves with a purple colour; when boiled with potassium dichromate the colour changes into brown or black.

Orange and Yellow Colours.

*Yellow aurin* on a tissue is changed, when boiled with soap, into a reddish shade; washing with water restores the colour. Dilute alkalies discharge the colour, a magenta-red solution being obtained. Lime water is coloured pink by it.

*Annotta* is changed into a bluish-green by boiling sulphuric acid; this test is best effected by exhausting the colour with alcohol, evaporating solution to dryness, and treating the residue with the acid.

*Picric Acid.*—The wool or silk is exhausted with hot dilute ammonia, and the deep-yellow solution concentrated on a water bath; on adding potassium cyanide to the residue, a blood-red colour is produced.

*Naphthalene yellow* gives almost the same reactions; but it can be distinguished from picric acid by heating with ammoniacal copper solution and washing. The colour of naphthalene yellow is then changed into olive green, and picric acid into bluish green.

*Turmeric* becomes brown by moistening it with dilute soda; acids restore the colour. On moistening the colour with a solution of boric acid, and drying, it becomes orange; and by treating it now with dilute soda it becomes blue, which soon changes into a dirty grey.

*Fustic.*—When boiled with aluminium sulphate, a yellow solution is obtained, showing a strong bluish-green fluorescence. The colour becomes very dark by treating it with a dilute boiling soap-solution, while *quercitron*, *Persian berries*, *and weld* do not change; but on boiling with stannous chloride, then the colour changes into orange.

(2) Blue Colours.

*Aniline* or *Phenyl blue* gives the same reactions as phenyl violet. The colour is soluble in boiling alcohol and acetic acid, and is discharged by bleaching powder. It is not dissolved by boiling aluminium sulphate.

Aniline blue is often mixed with indigo or indigo-sulphuric acid. To analyze such a mixture boil the tissue with alcohol, which dissolves the aniline blue. Then boil the same portion with aluminium sulphate, which dissolves only the indigo-sulphuric acid. If the cloth still remains blue, it indicates the presence of indigo.

*Indigo* is neither changed by alkalies nor hydrochloric acid, nor soluble in hot alcohol, but dissolves a little in boiling glacial acetic acid. Bleaching powder discharges the colour.

*Indigo-sulphuric acid* is coloured brown or yellow by cold ammonium sulphide.

*Prussian blue* is not changed by acids, but readily by alkalies, the residue on the cloth consisting of ferric oxide, while the solution contains a ferrocyanide, which can be detected by adding hydrochloric acid and ferric chloride.

(3) Green Colours.

*Aniline* or *Iodine green* dissolves in strong hot alcohol. On boiling it with dilute hydrochloric acid it turns blue or purple. Potassium cyanide bleaches the colour.

The other green colours are generally mixtures of aniline or Prussian blue, or indigo, with yellow colours. They may be tested as follows:—

Boil with strong alcohol.

(*a*) The alcohol is coloured yellow and the tissue blue. Indigo or Prussian blue is present. The residue is washed and tested for these colours as already indicated. The alcohol is also tested for yellows as directed above.

(*b*) The alcohol is coloured green; aniline blue is present. Boil another part of the substance with dilute hydrochloric acid; it will change into blue, and a yellow solution is obtained, which is examined for the yellows.

*Black Colours.—Aniline black* is recognized by its peculiar velvety tint. It is not changed by alkalies; acids change it into a dark green; alkalies restore the colour. Bleaching powder turns it into a garnet red.

*Madder black* is tested like madder purple.

*Logwood black* leaves an ash containing either ferric oxide or chromic oxide. It is coloured red by hydrochloric acid, and blue on the subsequent treatment with aluminate of soda. Bleaching powder discharges the colour.

*Tannin black* leaves a residue of ferric oxide, and is discharged by hydrochloric acid; the residue gives neither the tests for logwood nor madder.

*Natural and Artificial Alizarin.*—J. Weber states that if the tissue is steeped in permanganate of potash, and then in an acid solution, the red produced by extract of madder turns a reddish-yellow, whilst that produced by artificial alizarin becomes a rose colour. Or, by treating the cloth successively with potassium dichromate and nitric acid, the madder red is discharged, whilst alizarin red still retains some colour. If then boiled in soda liquor of 18° Beaumé, washed, and dipped in hydrochloric acid at 20° B., alizarin red becomes a light yellow, but madder red a dirty orange.

The swatches are dipped in a solution of 1 gramme of permanganate of potash in 200 cc. of water, and are then washed, and plunged into hydrochloric acid at 3° B., again washed, and a second time dipped in the permanganate of potash, after which they are washed and passed through oxalic acid at 1° Beaumé. Or, the swatches are steeped in a solution containing 10 grammes of bichromate of potash in 200 grammes of water, drained, passed through nitric acid at 6° B., and washed.

Professor W. Stein has published the following analytical tables for the detection of the different organic colours on tissues:—

RED COLOURS.

<table>
<tr><th>Heat with Ammonium Sulphide.</th><th colspan="6">Boil with a Solution of Aluminium Sulphate.</th></tr>
<tr><td rowspan="2">The colour changes into greenish or bluish.</td><td>The liquid colours red, and shows a beetle green reflection.</td><td colspan="5">The liquid becomes red without showing a reflection. On adding an equal volume of acid sodium sulphite—</td></tr>
<tr><td>Aloes purple; may be confirmed by boiling with baryta water, which changes the colour into green. If at the same time the liquid becomes purple, archil is also present.</td><td>Madder.</td><td colspan="3">It is bleached</td><td colspan="2">It is not bleached</td></tr>
<tr><td></td><td></td><td colspan="3">Brazil wood, santal, magenta, corallin, safflower.</td><td colspan="2">Cochineal, lac-dye, kermes, archil.</td></tr>
<tr><td></td><td></td><td colspan="3">Boil with alcohol of 80 per cent.</td><td colspan="2">Boil with alcohol.</td></tr>
<tr><td></td><td></td><td>The liquid colours distinctly bluish red.</td><td>yellowish red.</td><td>Liquid colours but little or not at all.</td><td>Liquid becomes red.</td><td>Does not colour, or only faintly.</td></tr>
<tr><td></td><td></td><td>Magenta.</td><td>Santal; is changed by lime water to brown, and it colours hot acids red.</td><td>Brazil wood, corallin, safflower.</td><td>Archil.</td><td>Cochineal, lac-dye, kermes.</td></tr>
<tr><td></td><td></td><td colspan="2" rowspan="2"></td><td>Heat with lime water, which shows,</td><td colspan="2">Heat with baryta water.</td></tr>
<tr><td></td><td></td><td>No colour.</td><td>Red colour.</td><td>Liquid remains colourless.</td><td>Liquid becomes red.</td></tr>
<tr><td></td><td></td><td colspan="2" rowspan="2"></td><td>Safflower.</td><td>Brazil wood, corallin.</td><td>Lac-dye.</td><td>Cochineal, kermes.</td></tr>
<tr><td></td><td></td><td colspan="2">Heat with dilute sulphuric acid.</td><td colspan="2">Heat with lime water.</td></tr>
<tr><td></td><td></td><td colspan="2" rowspan="2"></td><td>Tissue colours orange.</td><td>Tissue turns yellow.</td><td>Tissue colours brownish red.</td><td>Tissue becomes violet.</td></tr>
<tr><td></td><td></td><td>Brazil woods.</td><td>Corallin. Copper chloride changes the colour into grey.</td><td>Kermes.</td><td>Cochineal.</td></tr>
</table>

## VIOLET AND PURPLE COLOURS.

### Heat with Ammonium Sulphide.

| Tissue is bleached. | Tissue colours brownish red. | Turns olive brown | Hardly any change. |
|---|---|---|---|
| *Soluble aniline violet, magenta with indigo carmine.* | *Mauve, Hofmann's violets.* | *Alcannet.* | *Archil, ditto with indigo, logwood, madder.* |

Boil with alcohol, which colours

| Violet. | Red. |
|---|---|
| *Soluble violet.* | *Magenta.* |

Add cold dilute hydrochloric acid, which colours

| Yellowish. | Purple. |
|---|---|
| *Hofmann's violet.* | *Mauve.* |

Boil with alcohol.

| Liquid colours pink or brown; ammonia changes it into violet. | Liquid remains almost colourless. |
|---|---|
| *Archil*, with or without *indigo*. If indigo is present, hot chloroform will colour blue. | Heat with dilute hydrochloric acid, which colours |

| Red. | Not, or yellow. |
|---|---|
| *Logwood*; if indigo be present, hot chloroform will colour blue. | *Madder.* |

## YELLOW COLOURS.

### Heat with a Dilute or Alcoholic Solution of Neutral Ferric Chloride.

The colour is not, or only very little, altered.

*Annotta, turmeric, aniline yellow, picric acid, naphthalene yellow.*

Place one drop of concentrated sulphuric acid on tissue.

| A blue or green spot is produced. | The spot becomes at once, or after some time, more or less brown or red. |
|---|---|
| *Annotta.* | *Turmeric, aniline yellow, picric acid, naphthalene yellow.* |

Add alcohol, with a few drops of hydrochloric acid and some boric acid.

Liquid colours

| Intensely pink. | Pale pink. |
|---|---|
| *Turmeric.* On adding an equal volume of water both liquid and tissue colour reddish-yellow. | *Aniline yellow.* Tissue colours violet, and on adding water, crimson; while the liquid assumes a deeper colour. |

No change

*Picric acid, naphthalene yellow.*

Heat with an ammoniacal copper solution, and wash.

Colour changes into

| Bluish-green. | Olive-green. |
|---|---|
| *Picric acid.* | *Naphthalene yellow.* |

Tissue colours more or less yellowish-green, olive-green, brown, or almost black.

*Madder yellow, fustic, fustet, quercitron, flavin, berries, weld.*

Boil with aluminium sulphate, and add an equal volume of water.

| Liquid becomes red, and has a green reflection. | Liquid yellow, with a bluish-green reflection. | Liquid yellow, without reflection. |
|---|---|---|
| *Madder-yellow*; contains tin as mordant. | Fustic. | *Fustet, quercitron, flavin, berries, weld.* |

Heat with baryta-water or lime-water.

| Tissue colours red. | Tissue colours a little darker. |
|---|---|
| *Fustet.* | *Quercitron, flavin, berries, weld.* |

Boil with glacial acetic acid; after cooling, the solution shows—

| A distinct green reflection. | No, or only a faint reflection, and is hardly coloured. |
|---|---|
| *English flavin.* The liquid is yellow. | Boil with basic lead acetate. |

| Colour of tissue scarcely changed. | Tissue colours orange-brown. |
|---|---|
| *Weld.* | *Quercitron, berries.* |

## BLUE COLOURS.

Heat with alcohol of 80 per cent., and a few drops of hydrochloric acid.

| Liquid and tissue become red. | Tissue remains blue; liquid colours blue. | No change. |
|---|---|---|
| *Logwood.* | *Aniline blue*, or *indigo-sulphuric acid.* | *Indigo*, or *Prussian blue.* |

Put one drop of strong sulphuric acid on the tissue.

| No change. | Colour changes into a yellowish or reddish brown. |
|---|---|
| *Indigo-sulphuric acid.* | *Aniline blue.* |

Heat with a solution of sodium carbonate.

| No change. | Colour becomes yellow or brown. |
|---|---|
| *Indigo.* | *Prussian blue.* |

## GREEN COLOURS.

I. Boil with a moderately concentrated solution of potassium cyanide.

| Colour changes into brown or yellow. | Does not change, or changes into a brownish or yellowish green. |
|---|---|
| *Aniline green, green* containing *indigo-sulphuric acid (carmine green).* | *Green*, containing *indigo* with or without *carmine green.* |

II. Add to solution thus obtained an equal volume of water, and then a solution of aluminium sulphate, until an abundant precipitate is formed; but avoid an excess. Filter and wash.

| Filtrate is yellow or reddish. | Filtrate is blue; precipitate after washing is :— | | Filtrate colourless, precipitate yellow. | Filtrate blue. |
|---|---|---|---|---|
| *Aniline green.* | Colourless. | Yellow. | Only *indigo.* | *Indigo-sulphuric acid.* |
| | *Carmine green*, with *picric acid.* | *Carmine green*, with a *vegetable yellow.* | | Precipitate is— |
| | | | | Colourless: *Picric acid.* / Coloured: *Vegetable yellow.* |
| | III. Dissolve yellow precipitate in water, add a little sulphuric acid, and filter. | | | Proceed as in III. |
| | Solution has a green fluorescence. | No fluorescence. | | |
| | *Fustic.* | *Weld, turmeric.* | | |
| | | Heat another portion with alcohol, add boric and hydrochloric acids. | | |
| | | Liquid colours. | | |
| | | Pink: *Turmeric.* / Not: *Weld.* | | |

BIBANOW has also lately investigated the reactions of similar colours—viz., HOFMANN'S violet, Paris violet, dimethylaniline-violet, diphenylamine-blue, methyldiphenylamine blue, iodine green, dimethylaniline green, saffranin, and magdala red.

With these colours he dyed patterns of silk, wool, and cotton. The silk was not mordanted, excepting that dyed with iodine green, which was fixed by tannin. The wool was also only mordanted with sulphur (*i.e.*, sodium hyposulphite and dilute sulphuric acid) for dyeing the two greens. The mordants for cotton were tannin and albumin. Diphenylamine- and methyldiphenylamine- blue were dyed in an alcoholic solution without mordants. The reagents which BIBANOW used were—acetic acid of spec. grav. 1·056; hydrochloric acid of spec. grav. 1·160; nitric acid of spec. grav. 1·245; chromic acid solution (1 : 20); caustic soda of spec. grav. 1·085; solution of sodium sulphide (1 : 10); solution of stannous chloride (1 : 10); solution of ferric chloride

(1 : 10); solution of bleaching powder (1 : 10), and common ammonia.

He moistened by means of a glass rod the different samples, and after some time washed them with water. In the following tables, the sign O means that no change has taken place.

HOFMANN'S VIOLETS.

| Reagents. | Cotton Mordanted | | Wool. | Silk. |
|---|---|---|---|---|
| | With Albumin. | With Tannin. | | |
| | Fine oluish violet. | Same. | Same. | Dahlia purple. |
| Acetic acid. | Blue, after washing, original colour. | Same. | Same. | Same. |
| Hydrochloric acid. | Pale yellow; on the margin green or blue; on washing, green, blue, and at last violet. | Same. | Same. | Same. |
| Nitric acid. | Pale yellow; on washing, blue, green, and violet. | Same. | Pale yellow. | Same. |
| Chromic acid. | Yellowish-brown; on washing, pale violet. | Same. | Brown. | Brown. |
| Soda. | Gradually a dirty grey; after washing, pale violet. | Brown; after washing, light grey. | Brown; washing restores the original colour. | Violet, then reddish violet; washing restores the colour. |
| Ammonia. | O | O | O | O |
| Sodium sulphide. | Gradually changed into light grey. | Same. | Gradually bleached. | Gradually bleached; on washing again, violet. |
| Stannous chloride. | Blue; after washing, pale violet. | Greenish blue; after washing blue. | Blue. | Blue; after washing, violet. |
| Ferric chloride. | Blue; after washing, original colour. | Bluish-green; after washing, black. | O | Blue; after washing, violet. |
| Bleaching powder. | Gradually bleached. | Same. | Slowly changed into pale grey. | Same. |

POIRIER'S METHYL VIOLET.

| Reagents. | Cotton Mordanted | | Wool. | Silk. |
|---|---|---|---|---|
| | With Albumin. | With Tannin. | | |
| Acetic acid. | O | O | O | O |
| Hydrochloric acid. | Pale yellow, with green and blue margin; on washing, bluish-green and then violet. | Same. | Same. | Same. |
| Nitric acid. | Pale yellow; on washing, green, blue, and then violet. | Same. | Same. | Same. |
| Chromic acid. | Yellowish-brown; after washing, pale yellow. | Same. | Same. | Same. |

POIRIER'S METHYL VIOLET—(*Continued*).

| Reagents. | Cotton Mordanted | | Wool. | Silk. |
|---|---|---|---|---|
| | With Albumin. | With Tannin. | | |
| Soda. | Gradually light brown; after washing, pale violet. | Brown; after washing, pale violet. | Brown; after washing reddish-violet. | Gradually pale grey; after washing, original colour. |
| Ammonia. | 0 | 0 | 0 | 0 |
| Sodium sulphide. | Pale grey. | Same. | Gradually bleached. | Gradually pale grey; after washing, violet. |
| Stannous chloride. | Blue; after repeated washing, violet. | Blue. | Blue. | Blue. |
| Ferric chloride. | Green; after washing, original colour. | Black. | Greenish grey; after washing, original colour. | Blue; after washing, original colour. |
| Bleaching powder. | Bleached. | Same. | Slowly bleached. | Gradually bleached. |

POIRIER'S DIMETHYLANILINE VIOLET.

| Reagents. | Cotton Mordanted | | Wool. | Silk. |
|---|---|---|---|---|
| | With Albumin. | With Tannin. | | |
| | Bright purple. | Bright purple. | Violet, with a faint greyish tint. | Rich purple. |
| Acetic acid. | 0 | 0 | 0 | 0 |
| Hydrochloric acid. | Pale yellow; margin green or blue; on washing, green, blue, and at last, violet. | 0 | Same. | 0 |
| Nitric acid. | Pale yellow; on washing, green, blue, and violet. | Same. | Pale yellow. | Like cotton. |
| Chromic acid. | Yellowish-brown; after washing, pale yellow. | Same. | Yellowish brown. | Brown. |
| Soda. | Gradually pale brown; after washing, pale violet. | Brown; after washing, pale violet. | Brown; after washing, violet. | Gradually greyish violet; washing restores the original colour. |
| Ammonia. | 0 | 0 | 0 | 0 |
| Sodium sulphide. | Pale grey. | Pale grey. | Gradually bleached. | Gradually pale grey; washing restores the colour. |
| Stannous chloride. | Blue. | Blue. | Blue; washing restores the colour. | Same. |
| Ferric Chloride. | Greenish blue; washing restores the colour. | Greenish blue; after washing, black. | Grey; washing restores the colour. | Greenish-blue; washing restores the colour. |
| Bleaching powder. | Gradually bleached. | More quickly bleached. | Slowly, but completely bleached. | Same. |

## DIPHENYLAMINE BLUE.

| Reagents. | Cotton, dyed in an Alcoholic Solution. | Wool. | Silk. |
|---|---|---|---|
| | Greyish-blue. | Blue, with a greyish tinge. | Same. |
| Acetic acid. | 0 | 0 | Colour more bright. |
| Hydrochloric acid. | 0 | 0 | 0 |
| Nitric acid. | Gradually grey. | Dark, dirty green. | Yellowish grey. |
| Chromic acid. | Greenish-yellow; after washing, grey. | Brown; after washing, greenish-yellow. | Greenish-yellow. |
| Soda. | Gradually discoloured; washing restores the colour. | Very slowly changed into grey. | Like cotton. |
| Ammonia, sodium sulphide, and stannous chloride. | 0 | 0 | 0 |
| Ferric chloride. | Green; washing restores the colour. | Same. | Same. |
| Bleaching powder. | Very slowly bleached. | Same. | Same. |

## METHYLDIPHENYLAMINE BLUE (PREPARED WITH OXALIC ACID).

| Reagents. | Cotton, dyed in an Alcoholic Solution. | Wool. | Silk. |
|---|---|---|---|
| | Beautiful blue. | Blue with greenish tinge. | Beautiful blue. |
| Acetic acid. | 0 | 0 | 0 |
| Hydrochloric acid. | 0 | Violet; washing restores the original colour. | 0 |
| Nitric acid. | Brownish-black; after washing, dark green. | Brownish-black in reflected light, and a dark reddish-violet in transmitted light; after washing, dirty blue. | Like wool; but after washing, yellowish-green. |
| Chromic acid. | Same as nitric acid. | Same; after washing, dirty blue. | Black; after washing, dirty green. |
| Soda | Grey; after washing, original colour. | First, reddish-violet, then dirty orange, and at last yellow. | Reddish-violet; after washing, blue. |
| Ammonia. | 0 | Pale green; after washing, blue. | Same. |
| Sodium sulphide. | Colour becomes pale. | Green, greenish-yellow, pale yellow; on washing, blue. | Same. |
| Stannous chloride. | 0 | 0 | 0 |
| Ferric chloride. | Greenish-blue; washing restores the colour. | Green; washing restores the colour. | Same. |
| Bleaching powder. | Slowly, but completely bleached. | Gradually green; after washing, greenish-blue. | Changes gradually into yellowish-grey. |

up to 50 c.c. Heat now in a porcelain basin some water nearly to the boiling point; add one gramme of white best wool, and let it get thoroughly wetted; remove it with a glass rod, and add to the water 1 to 2 c.c. of the colour; mix well and dye the wool in this solution. When it has taken up all the colour, add gradually more until it attains the proper shade. Suppose now that 7 c.c. were required to produce the same shade as 5 c.c. of the standard colour, then the value of the colour will be $\frac{5}{7}$ of the standard.

In a similar way most other colours may be tested, as for instance, flavin, cochineal, &c. A proper dye-bath is made containing a given weight of colour; in a portion of it a given weight of wool is dyed, and gradually more colour is added until the proper shade has been attained.

If metric weights or measures are not at hand, grains and fluid grains are used. Thus in the above example 10 grains of the colour are dissolved in 100 fluid grains of spirits, and with this solution 20 grains of wool are dyed by adding gradually to the boiling water the solution of the colour, as described above.

**Calico Printing.**—Calico (from Calicut, a town in Northern India), is a kind of cloth made entirely from cotton; but the term calico printing has usually a broader meaning than simply printing calico, and is generally applied to the printing of any kind of tissue used for garments, whether made from cotton alone, or mixed with other fibres, or made of linen, wool, or silk.

*Historical.*—A few passages occur in ancient writers which, though vague and general, make it certain that there existed in very remote times, say 2000 B.C., some method of colouring cloth with designs representing figures of plants and animals; but it is only in Pliny that there is any distinct reference to the methods employed, and he describes in a dozen lines the dyeing of mordanted cloth, as seen by him practised in Egypt, in very much the same terms that an intelligent but non-technical observer might describe at this day the operations of a madder dye house. The only remains of ancient textile fabrics which have been preserved to modern times are the wrappings of mummies. These are shown to be made of linen, and not of cotton; and though Mr Thompson of Primrose proved tolerably well that both indigo and safflower had been used to dye some portions of mummy cloth, no appearances of printing have been discovered on these wrappings. All printed textile fabrics are in their nature so perishable and intrinsically of so little value, that it is not surprising that there are very few examples of them to be found bearing old dates. Nevertheless we are not quite without illustrations of respectable antiquity. In the South Kensington Museum there is a very early and rare specimen of block-printed silk of the thirteenth century, of Sicilian origin (No. 1251); there are also several specimens of Flemish block-printed linens ascribed to the fourteenth century; and an example of Byzantine printing on a mixed cotton and silk tissue of the same date. No doubt the art of printing or painting designs on cloth was always practised more or less in civilized communities where textile fabrics were manufactured; and we may conclude that in the middle ages Sicily, Italy, and Flanders were countries where the process was carried on, and whence it spread to other places. The introduction of calico printing into England was stated by Thompson to date from 1690, when a Frenchman, supposed to be one of the Huguenot refugees, established a small work on the Thames at Richmond. This statement was adopted by Baines in his history of the cotton manufacture, and is repeated with additions by Potter, Persoz, and every other writer upon this subject. But it will be seen that there are no grounds for this supposed introduction by a Frenchman, and that printing was practised in England at much earlier dates than 1690. The Edict of Nantes was revoked by Louis XIV. in 1685, and Dollfus Ausset, in remarking upon Thompson's statement, says that if it be true that the exiled Huguenots introduced printing into England or elsewhere, they must have learned their business somewhere out of France, for there were no printworks in France before the year 1746, when the Kœchlins established their firm at Mulhouse, and they received their knowledge of blocks and mordants from Hamburg. In the South Kensington Museum there is a specimen of English block-printed chintz of early date, No. 1622, and Canon Rock believes that still earlier specimens are to be found in the chapter library at Durham. The very earliest account known of printing shows that the art was practised in England before the year 1410; it is to be found in manuscripts preserved in the Bibliothèque Royal in Paris, some of which have been printed, and some translated by Mrs. Merrifield in her work on painting. In the manuscript of Jehan de Begue, under date of 11th February, 1410, there is an account in old French given by one Theodore, a native of Flanders, to Johannes Alcherius, of the composition of certain topical colours, which the said Theodore had himself made and used in England for painting upon cloth, probably of linen. These colours are composed of materials and would produce effects similar to those in use for low-class printing at this day; iron liquor, alum, brazil wood, kermes, walnut peel, galls, indigo, lime, honey, and orpiment are prescribed. None of the recipes give any thickening matters, and it may be gathered that these dyes were applied by a brush or pencil upon cloth prepared with gum water. The earliest English patent referring to printing is dated 1619, and there are others in 1675, 1676, and 1692, which clearly show that printing was a business well known and practised in England before the Huguenot exodus took place; this, with the previous evidence, leads to the belief that it was introduced into England from Flanders some time in the fourteenth century.

Like most other industries, that of calico printing had to struggle against mistaken fiscal regulations. Not only the importation, but the home manufacture of cotton prints, was for a time interdicted to serve

the interests of other manufactures. Later on, the printing of calico was permitted under a heavy duty, which was reduced eventually to 3½*d.* per square yard, equivalent to 5*s.* per piece on all the calico printed in the last year of the imposition of this duty, which was 1830, when the amount obtained was £1,897,265 7*s.* 1*d.* (Potter *On Copyright*, 1840.)

The history of calico printing from that date is to be found in the following pages in connection with the various processes and machines employed.

The practical treatment of the subject of calico printing as a manufacture may be conveniently divided into the following sections:—

1. Processes preparatory to Printing; these include marking, singeing, bleaching, and shearing, with winding on.

2. Printing Processes; including the various means by which the design is reproduced upon the cloth by pencilling, stencilling, block printing, and cylinder printing, with a few special methods.

3. Preparation of the colours for printing, embracing the routine of the colour house, and a study of thickeners and mordants.

4. Treatments of the cloth after printing, to fix or develop the colour, amongst which are ageing, steaming, chroming, &c.

5. Dyeing processes, including dunging, soaping, washing, and clearing.

6. Finishing processes, including starching, stretching, mangling, degging, and calendering.

*On the Marking of the Grey Calico.*—In the management of a print works, it is desirable to be able to trace backwards the course of any given piece of calico. To this end the first process is to stamp every lot of cloth with some number or distinctive mark. The best substance at present known is gas tar; most oil colours, as red lead paint, printers' ink, or common black paint can be used, and will leave sufficient traces upon the cloth after bleaching, but there is nothing known which will stand the bleaching processes in a perfect manner. Aniline black comes out perfectly distinct under favourable circumstances, but it is uncertain and unmanageable. In the last century Hausmann investigated the subject, and after trying copal varnish with pigments, which stood pretty well, recommended manganese salts fixed by alkali, as capable of withstanding all the bleaching operations. The application of a fixing agent would be highly inconvenient, and the process was probably never put into practice. Weft dyed in manganese brown has been used as a heading, but it is not permanent, often disappearing completely before the end of the bleaching.

*Sewing of the Pieces for Bleaching.*—A loose strong stitch is required. The quality of the thread is of importance; for the breaking out of an end in bleaching entails great loss of time and interruption to the process. Hard thread may cut the cloth in the squeezers, and should be avoided.

Singeing.—This is the first manufacturing operation in a print works. It is known also under the names of firing, dressing, and perhaps some others; the object is to remove the numerous ends of cotton hairs which can be seen when a piece of grey calico is held on a level with the eyes. If these hairs were left on they would interfere seriously with the printing operations. A well-singed cloth receives the colours impressed upon it directly on the warp and weft threads which form the tissue; and nothing short of the turning of these threads in the after operations will disturb the clear outline and uniformity of shade of the finest line. On an unsinged cloth the result is different; the colour is deposited in part upon the shifting hairs. So long as these hairs remain where the printing operation has fixed them no considerable defect is to be observed; but when the cloth comes to be wetted, the hairs float about to the extent of their tether, and upon drying occupy different places—the coloured ones lying over the white, and the white ones over the coloured places of the print, blurring the outline, and destroying all clearness and sharpness of effect. In dark-ground prints defective singeing is very injurious, since it usually happens that the unsinged hairs are less coloured than the body of the cloth, and destroy the uniformity of the dark colour. Nevertheless there are some styles of coarse prints in which it is nearly indifferent whether the cloth be singed or not, and there are other styles in which a good full face on the calico is more valued than clearness of outline. For such styles singeing may be omitted, but for all better class styles it is indispensable.

No mechanical method of removing these hairs in a satisfactory way has been discovered; they have not sufficient resistance to be cut off by any shearing process; and as the term *singeing* expresses, they are burnt off by some one of the arrangements afterwards to be described. The methods of singeing are—(1), by red-hot plates; (2), by flame of gas, alcohol, or other combustible; and (3), by a combination of flame and red-hot plate. The ordinary singeing stove consists of a long and narrow fire-grate, covered over with a copper plate, which is bent to a curvilinear form; the fire heats this plate red hot, and the cloth is drawn over it, and in contact with it, in a swift and regular manner. A drawing of a singe plate is given at p. 367, Bleaching. One passage over such a plate does not generally singe cloth sufficiently well. If the plate could be kept at a uniform bright red heat, a single passage might be enough; but that is hardly possible on account of the rapid cooling action of the cloth upon the metal, which soon reduces the temperature below the singeing point. When the plate is long enough to allow the cloth to be traversed from the cooled part to a hotter part, and then back again, something can be done by a skilful man; but the general result of such treatment is uneven singeing, one edge of the piece singed and the other half singed. And yet it is very undesirable to singe twice over, on account of not only the labour, but the danger of fire. To meet this difficulty two plates can be arranged side by side, and may be heated by the same fire, either directly, or the flue from the fire under one plate can be led round under the other; in this case, one plate is usually much less heated than the other.

## IODINE GREEN.

| Reagents. | Cotton Mordanted | | Wool. | Silk. |
|---|---|---|---|---|
| | With Albumin. | With Tannin. | | |
| | Bright green. | Somewhat bluish-green. | Bluish-green. | Very pure green. |
| Acetic acid. | Bluish-green. | Bluish-green. | O | Bluish-green; washing restores the colour. |
| Hydrochloric acid. | Yellow; after washing, green. | Same. | Same. | Same. |
| Nitric acid. | Like cotton. | Same. | Yellow. | Yellow. |
| Chromic acid. | Yellowish-brown; after washing, pale yellow. | Same. | Same. | Same. |
| Soda. | Pale yellow; after washing, colourless. | Same. | Same. | Same. |
| Ammonia. | Bluish-green. | Same. | Paler. | Paler. |
| Sodium sulphide. | Bleached. | Same. | Same. | Same. |
| Stannous chloride. | Yellowish-green. | Same. | O | O |
| Ferric chloride. | Yellowish-green; washing restores the colour. | Black. | O | Black (tannin being present). |
| Bleaching powder. | Gradually bleached. | Same. | Incompletely bleached. | Gradually bleached. |

## DIMETHYLANILINE GREEN.

| Reagents. | Cotton Mordanted | | Wool. | Silk. |
|---|---|---|---|---|
| | With Albumin. | With Tannin. | | |
| | Pale greyish-green. | Bright green. | Bluish-green. | Bright green. |
| Acetic acid. | Bluish green. | Same. | O | Bluish-green. |
| Hydrochloric acid. | Yellow; after washing, green. | Same. | Same. | Same. |
| Nitric acid. | Like hydrochloric acid. | Same. | Yellow. | Yellow. |
| Chromic acid. | Yellowish-brown; after washing, pale yellow. | Same. | Yellowish-brown; after washing, greenish-yellow. | Same as wool. |
| Soda. | Flesh-colour, then pale yellow; after washing, almost colourless. | Same. | Colour becomes very much paler, and disappears on washing. | Like cotton with albumin. |
| Ammonia. | Paler. | Paler. | Colourless; after washing, green. | Paler. |
| Sodium sulphide. | Bleached. | Bleached. | Only completely bleached after washing. | Same as wool. |
| Stannous chloride. | Yellowish-green; colour restored by washing. | Yellowish green. | O | Yellowish-green. |
| Ferric chloride. | Like stannous chloride. | Black. | O | Like cotton with albumin. |
| Bleaching powder. | Bleached. | More slowly bleached. | Only slowly and incompletely bleached. | Gradually bleached. |

SAFFRANIN.

| Reagents. | Cotton Mordanted | | Wool. | Silk. |
|---|---|---|---|---|
| | With Albumin. | With Tannin. | | |
| | Beautiful, but not intense crimson. | Intense crimson. | Intense crimson. | Beautiful, but not intense crimson. |
| Acetic acid. | Colour becomes brighter, but after washing it appears unaltered. | Same. | 0 | 0 |
| Hydrochloric acid. | Blue, after washing red again. | Same. | Same. | Same. |
| Nitric acid. | Like hydrochloric acid. | Same. | Same. | Same. |
| Chromic acid. | Yellowish-brown. | Same. | Same. | Yellowish-red. |
| Soda. | 0 | 0 | 0 | 0 |
| Ammonia. | 0 | 0 | 0 | 0 |
| Sodium sulphide. | Yellowish-red; after washing, original colour. | Yellowish-brown. | 0 | 0 |
| Stannous chloride. | Yellowish; after washing, pale red. | 0 | 0 | 0 |
| Ferric chloride. | Yellowish-brown; after washing, red. | Blackish-brown. | 0 | 0 |
| Bleaching powder. | Brown, grey, yellow, and at last colourless. | Same. | 0 | Gradually bleached. |

MAGDALA RED.

| Reagents. | Cotton Mordanted | | Wool. | Silk. |
|---|---|---|---|---|
| | With Albumin. | With Tannin. | | |
| | Bright pink. | Pink, having a faint purplish tinge. | Like cotton, with tannin. | Bright pink. |
| Acetic acid. | 0 | 0 | 0 | Colour more vivid; but after washing, original shade. |
| Hydrochloric acid. | 0 | 0 | 0 | Brighter. |
| Nitric acid. | Grey, yellowish-grey, yellowish; after washing, yellowish-red. | Same. | Grey, then yellowish; after washing, yellow. | 0 |
| Chromic acid. | Yellow; after washing, pale. | Same. | Yellow. | Yellow. |
| Soda, ammonia, sodium sulphide, and stannous chloride. | 0 | 0 | 0 | 0 |
| Ferric chloride. | Brown. | Black. | 0 | 0 |
| Bleaching powder. | Quickly bleached. | Same. | Gradually bleached. | Same. |

The two samples of cotton were dyed in an alcoholic solution.

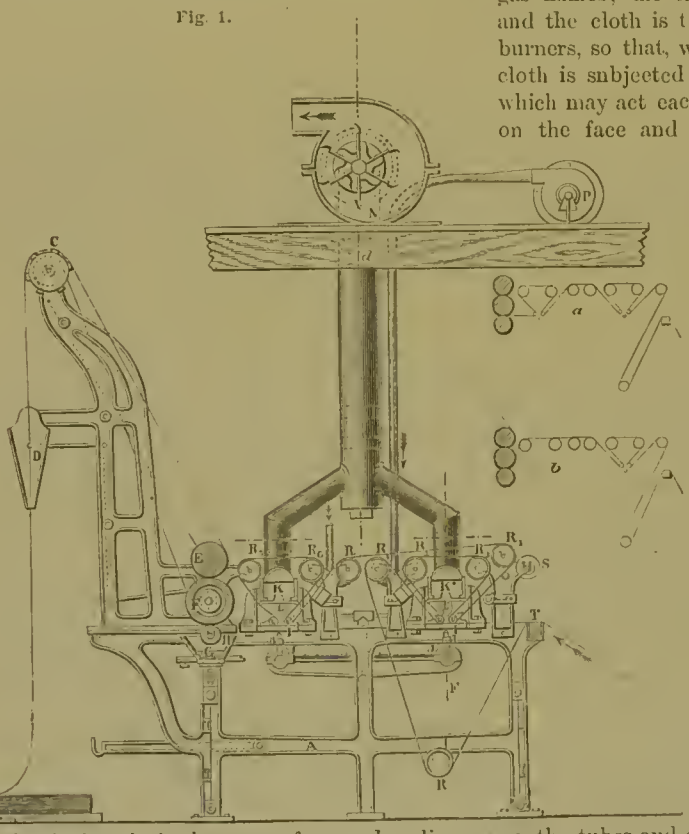
The most practical method of estimating the value of a dye stuff, is to dye a certain given shade on a weighed quantity of wool, silk, or cotton, and compare the quantity of colour used with a standard colour.

Thus an aniline colour may be tested in the following way:—

5 decigrammes of the colour are dissolved in warm spirits of wine, and when cold, the solution is made

The best arrangement is to heat each plate by a separate fire, so that both can be kept at a proper singeing heat. For it is probable that passing the piece across a dull red or, as it often occurs with bad stoves, over a black plate, does no good at all, but rather harm, by flattening down the hairs, which are then not so readily burned by the second plate. The speed with which the cloth should pass across the plates depends upon the degree of heat of the plates, and provision should be made for varying the speed. The most convenient way of doing this is by driving with an independent small engine, but there are other well-known means of doing it from gearing. Two plates in good order will singe cloth at the rate of from 120 to 150 yards per minute, two pieces in width being singed at the same time. A singe of this description answers for good ordinary prints. But sometimes much more labour and care is given to the singeing. In the case given, only one side of the piece is singed, but many singe both sides, and sometimes the cloth is sent three times across the plates—twice on the side intended to be printed, and once on the back of the piece.

Fig. 1.



*Gas Singeing.*—Soon after the introduction of gas for illuminating purposes it was applied to singeing calico. Hall's patents are dated 1818 and 1823; his process consisting in drawing the cloth through a gas flame, the action of which was assisted by a chimney over the flame. Many modifications of the original plan were carried into practice, but without any marked success. The chief complaint was, that when the cloth was fairly well singed, it was at the same time much impoverished, owing to the gas flame penetrating the tissue and burning the threads, making them thinner and weaker. It was evident that this could be prevented by making the cloth pass over, and in close contact with, a metallic surface while the gas flame played against it. The difficulty here consisted in getting a proper combustion of the gas, and this was attempted more or less successfully by mixing air with the gas. Probably the best arrangement for singeing yet produced is that of Tulpin, Fig. 1, patented in England in 1862. It consists essentially of two rows of ordinary gas-burners, each row the width of the piece to be singed. The cloth is brought in contact with the flame by means of two metal rollers of small diameter, and near to one another, one on each side of the row of gas flames; the flame passes between the rollers, and the cloth is twice singed by each row of gas-burners, so that, with two rows of gas-burners, the cloth is subjected four times to the singeing flame, which may act each time on the same side, or twice on the face and twice on the back. The steady burning of the gas is secured by an exhaust fan, P, properly connected with the burners by tubes, and the products of combustion are at the same time carried away in a very perfect manner.

Fig. 1 shows the construction of this apparatus, and how it may be threaded to give different kinds of singeing. The rows of gas burners are supported on the arm, J J, which can be raised or lowered as required. The flame of the gas passes between the small metal rollers, U, U, U, U, which are provided with an adjustment permitting the distance between each pair to be increased or diminished. The products of combustion, along with detached carbonaceous matters, are carried upwards into the hoods, K and K′, which extend the whole width of the machine, whence they are drawn by the action of the fan, N, up the tubes and expelled into the external air. In the machine as shown the cloth is entering in the direction of the arrow over the scrimp bar, T, then passing under the roller, $R$, and over $R_1$ down to the metal roller, U″, where it first comes into contact with the gas flames; then passing over the rollers, $R_2$ and $R_3$, and down to the small metal roller, U‴, it passes a second time, and on the same side, through the flame; then carried by the rollers, $R_4$ and $R_5$, down to the second pair of small metal rollers, it comes into contact with the flame of the second row of gas-burners, but exposing the reverse side of the piece to its action. By the rollers, $R_6$ and $R_7$, it is led again to the flame, and is a second time singed on the reverse side, and passing between the roller, H, which is kept wet by water in

the trough, G, and the draw roller, E, it is taken by the wince, C, and laid down in folds by the plaiter arm, D. It will be seen by this system of threading that the cloth is singed twice on the face side and twice on the reverse side. The outline at *a* shows how the cloth can be threaded so as to be singed four times on one side, and in the arrangement *b* the cloth is singed twice only on one side.

*Singeing by Flame and Plate Combined.*—In 1862 a patent was granted to Eddleston and Gledhill for an apparatus to singe cloth by means of flame arising from burning coke or other combustible. The arrangement consists of a narrow furnace of fire-brick, open above, and so closed below that a blast from a fan or blower travels through the burning coke and produces a large flame above. The cloth to be singed is drawn over or through this flame by ordinary contrivances. When the furnace is in good condition and burning coke, a voluminous and smokeless flame is produced, which, when playing against the cloth, covers several feet of it at once. It would appear that this system of singeing was first intended for woollen goods, and when applied to cotton cloth was found deficient in power; but at this time it is used in conjunction with a copper-plate singeing furnace, and said to give good results—the cloth passing first over or through the coke flame, and then immediately over the red-hot plate. The passage through the flame evidently dries and warms the cloth, as well as singes off the longer hairs; and the single plate, working after the coke flame, can, it is said, be easily kept at a good singeing heat all the day; and thus the chief difficulty in singeing by the plate is avoided. Of course this is only another way of using gas, but probably the most economical way that could be devised; and when coke is the fuel employed, there can be no carburetted hydrogen in the gas, and consequently no smoke and no discolouring of the cloth by soot. For a drawing of the furnace, but not in conjunction with the singeing plate, see the patent. No. 197, January 25, 1862.

Of these three methods of singeing, it is difficult to say which is preferable. Gas is much cleanlier, and, on the whole, freer from danger of fire than the plate; but it is generally more expensive, and, as far as my experience goes, never so thorough or complete in its action. With Tulpin's machine, and probably with other gas machines, a very fair singe can be got, and it is easily managed and pleasant to work with; but the writer had every opportunity of comparing it with goods singed by two plates, and preferred the latter. In Eddleston and Gledhill's patent, whatever may be its merits practically, there seems no doubt that it is the plate which does the singeing, the flaming only preparing for and helping the plate. Tulpin's machine, according to a paper by Schultz (*Bull. de Mulh.* 37, 533), was tried at Steinbach-Koechlin's at Wesserling; 1000 mètres of calico required, in one trial, 1331 litres of gas, and in another, 1180 litres. In a trial near Manchester, 25,000 yards of calico were singed in seven hours, with a consumption of 1330 cubic feet of gas—the French experiment taking somewhat less gas than the English. At Wesserling the opinion was, that there was not much difference in the expense between gas and plate singeing; but that is a question depending upon the relative prices of gas and fuel. In other places the gas cost three times as much as the plate. In the plate-singeing, the wearing out of the plates is a large item of the expense. There is a great difference in copper plates: some wear away much quicker than others. One plate that I noted singed 2,100,000 yards of calico before it was taken out. With careless firing and with sulphurous coal plates are soon worn out. One pound of coal can singe from 80 to 120 yards of calico of narrow width.

*General Remarks upon Singeing.*—Whichever method of singeing be adopted, there are some general points to be attended to. While endeavouring to get as perfect a singe as possible, it is evident the cloth must not be burned or over-singed. Double edges are liable to be burned, on account, probably, of being pressed closer to the plate than the body of the cloth. If the plate is much worn in the middle, the two edges of the cloth are liable to be injured; and if the plate becomes much thinner in one part than another, that part will be much hotter than the rest. Fire must be carefully guarded against. Ends of threads, and knots from defective weaving, and ends of the sewing thread, are particularly liable to carry over sparks; and in dry singeing, as for back greys, some contrivance must be adopted to extinguish them. The best plan is to pass the goods through a box where a good jet of steam from a perforated pipe plays against the whole width of the piece, and keeps the box full of steam, and consequently cools down the piece; and by excluding atmospheric air, generally extinguishes all sparks. To secure this a strong current of steam is required: a feeble, low pressure is of little use. After making all allowances for the possibility of sparks, there are cases of goods firing which seem due to spontaneous combustion. If a spark is unextinguished, and carried over with hot cloth, it will cause fire in a few minutes; but there are cases where the fire has not developed itself until some hours after the goods were laid down. It is quite conceivable that some spot of grease or flour size, or other foreign matter on the cloth, is the origin of such a fire without any actual sparks being there. It should always be remembered that the calico after singeing is very hot and dry, and therefore liable to take fire from the smallest sparks. If there is a good ventilation in the singeing stove, and a hood to carry off the fumes and sparks, little danger can arise from floating sparks; but no one can be too careful of the very inflammable fluffy matter which collects about the brickwork, and some of which is occasionally carried on to the piece. In fact, dry-singed goods cannot be considered safe until they are cool; and wherever it is possible should be cooled by running over a series of rollers, or by being pulled over a rail.

Goods which go straight on to the bleachhouse

are efficiently protected from fire by being made to pass through a trough of water, and between rollers which are lapped with some stuff which is kept saturated with water.

Good printer's cloth is now woven with very little size in it; but not very long ago managers were liable to be troubled with cloth containing 20 or 30 per cent. of flour size, and this is a great hindrance to singeing. It cakes upon the plate and cakes upon the cloth, and causes many stoppages and inconvenience, and in fact cannot be properly singed. In passing judgment upon the singeing, it must not be forgotten that some kinds of cloth have much more face on than others (a printer's cloth ought to have no face on), and are much more difficult to singe clean, and that cloth from low, short-stapled cottons, even if it be well singed, seems nearly as bad as ever after bleaching. This remark leads naturally to the question of why not singe after bleaching, instead of before? For the calico is knocked about a good deal in the process of bleaching, and many ends of hairs are loosened by the necessary movements of the cloth, undoing, as it were, what the singeing had done for it. The only reason is the discoloration of the white which would take place by the carbonaceous particles of the charred hairs adhering to the fabric; and though this discoloration is of a mere physical or mechanical pigment, it cannot be removed except by vigorous treatments, which would again leave the cloth as bad as before, or nearly so. But practically it is not unusual to singe after bleaching for particular styles where a slight discoloration of surface is of no consequence, as in dyed and soaped styles; or sometimes as in heavy dark blotches, the goods are singed after dyeing even, to remove the white hairs which, if left on, make this style so unsightly. But this after-singeing is additional to the first singeing, and should be done with gas or coke flame, so as to reduce the discoloration of the white to a minimum amount.

Bleaching for Calico Printing.—The next step after singeing is bleaching. This word means whitening, but in calico printing it has a wider signification; it means a thorough cleaning and purifying of the cloth from extraneous matters. It is an operation of the utmost importance: for with a well and soundly bleached cloth to work upon, all styles of printing may be attempted with hope of success; but against bad bleaching it is vain to contend. The best skill and the best materials are thrown away upon badly bleached cloth, and irregularity and inferiority will pervade every result. It is therefore a subject which demands all the attention and consideration which can be bestowed upon it.

The bleaching arrangement which is now almost exclusively employed is called "the continuous process;" the whole number of pieces of calico to be treated are sewn end to end, forming one or two unbroken lengths of cloth, which may extend from fifteen to forty miles, according to the quality and width of the calico and capacity of the kiers or boiling vessels. The ends of the pieces are not sewn until the bleaching operations are quite finished, and this is all that is meant by the term continuous, for in practice the operations are intermittent, and the cloth is laid down and taken up many times in the course of the bleaching. The number and purposes of such movings of this long riband of calico are here shown in tabular arrangement, and each one may be considered as a distinct step in the bleaching, and naturally subdividing the subject into so many heads.

1. Wetting out and steeping of the calico in water.
2. First washing.
3. Liming and boiling with lime.
4. Washing out of the lime.
5. Souring or acid treatment after lime.
6. Washing out of the acid.
7. Boiling with soda ash and rosin.
8. Washing out of the soda-ash.
9. Treating with bleaching liquor or chloride of lime.
10. Souring after chloride of lime.
11. Final washing and drying.

*Wetting out, Steeping, Rot Steep.*—The first operation is to impregnate the goods thoroughly with water. This is usually done in conjunction with the singeing, and has for its chief object the softening and loosening of the starchy matters contained in the calico. Ordinary grey calico repels liquids so strongly, that a bit may be dipped in water and removed almost without being wetted. It may be observed, that if calico singed on one side is passed quickly through water, the singed side takes the water pretty well, while the other side is scarcely moistened. A second object in washing out is to prevent this temporary impermeability from producing irregularity in the liming, which would certainly take place if the grey cloth was passed into it without previous treatment. The older bleachers attached much importance to the steeping of the calico, which from the fermentation, or one might say putrefaction, which was set up in the mass, was generally called the rot steep. They believed that good results could not be obtained if the pieces were moved before a pretty active fermentation had taken place, and to insure this bran and other easily fermentiscible bodies were mixed with the water to promote the desired action.

They were probably right in their time, for they had to deal with a printer's cloth of a very different kind to that now supplied, and they had not the means of giving the effective subsequent treatments which were afterwards discovered. The displacement of hand-loom cloth, with all its abominations of domestic sizing, by the cleaner power-loom calico, and the gradual simplification of the sizing of this latter, combined with a more rapid transfer from the loom to the bleachhouse, have done much towards making bleaching easier and more certain than it was formerly.

At the present time an enlightened bleacher attaches no importance to fermentation, except to carefully avoid too much heating of the wetted cloth when circumstances have compelled him to leave it in a heap longer than necessary, and if it becomes heated, to cool it down either by moving it or by application of cold water. Grey calico, but slightly wetted, may become much injured from

heating; if entirely submerged in water there is little or no fear of its becoming heated to a dangerous point. While there is an undoubted advantage in leaving the cloth several hours in steep, there is no absolute necessity for it; and if the routine of operations require it, the thoroughly wetted cloth may be at once passed on to the washing machine. Since it was discovered that diastase, which exists in a decoction of malt, had the property of rapidly transforming starch into soluble gum-like compounds, it has been proposed to use it in the steeping water; but even if effective, it is expensive and unnecessary.

*First Washing.*—The object of this washing is to remove whatever is soluble in water, or can be detached by agitation in it. These matters are mainly the weaver's size or a portion of it, and the salts which may have been added to it, as acetate of lead, sulphate of copper, with glycerine, and probably soap, and the soluble saline constituents of the cotton proper, which are very small in amount. The washing is not pushed far, for no practical time or quantity of cold water would remove all these matters; the bleacher is content just to take off what comes away easily, and what might form an obstruction to the liming. Whatever washing machine may be employed, it is advisable to give the cloth a good squeeze as it leaves it, so that as little water as possible may remain in; for well squeezed cloth, or if squeezing is not practicable, well drained cloth, is easier to lime than very wet cloth.

*Application of the Lime to the Cloth.*—Lime is nearly insoluble in water. The milky fluid called milk of lime consists of particles of hydrate of lime mechanically suspended in lime water. If the milk of lime is left at rest, these particles soon subside and leave a clear liquid, which contains but a small quantity of lime—not more than one part in weight to 700 parts of water: a fluid far too weak for bleaching purposes. That a sufficient quantity of lime may be applied to the cloth, it has to be used in the milky state, and care must be taken that it is applied with tolerable uniformity to the mass of cloth to be bleached. Formerly the lime was thrown on the cloth as it was deposited in the boiling kier by buckets or scoops, or run in by a spout. An improvement was to play the milk of lime upon the cloth with a hose pipe and nozzle; but these plans were defective, on account of the irregular and unequal distribution of the lime: some parts got an excess and some too little. A uniform impregnation is easily obtained by means of the modern liming machine, the cloth passing through a box or cistern of milk of lime on its way to the kiers, and the excess being squeezed out by pressure-rollers. It is well to have the lime slacked some time before it is wanted, to insure the perfect absorption of the water by the lime, and the absence of any bits of unslacked lime. Lime slacked to the consistence of a paste that can be taken up with a spade will keep good for a long time, if it is in pits where it will not dry, and is not much exposed to the air. In this state it is well adapted for bleaching. But it is not always convenient to connect such places with a bleachhouse; and lime will not run through small pipes, nor can it be pumped satisfactorily; therefore the slacking is generally done in the bleachhouse or close to it, so that the milk of lime can run to the liming machine through a spout or culvert by its own gravity. But still there should be no difficulty here in having a reserve, so that the lime for a boiling should be slacked at least twelve hours before it is wanted.

During the liming the milk of lime must be kept in constant agitation, or its strength will vary very materially. This can be done by hand, or preferably by a mechanical stirrer. If the lime is of a quality that slacks well—that is, fine and soft—it may be nearly all used up, except the stones and unburnt pieces; but there are some kinds of lime which give a large portion of a heavy, granular hydrate, causing much waste; for it is no use stirring the lime so violently as to bring up these heavy particles: they either settle in the trough or at the bottom of the liming box, and do not get on the cloth at all, or if the cloth takes them up, it is in an irregular manner. A good milk of lime has a translucent appearance in thin layers by reflected light, as, for example, when seen running down a trough into the machine. An opaque, starchy-looking milk of lime is to be feared as weak and inactive.

The length of time which the cloth is in contact with the milk of lime in the machine must depend on circumstances. A great deal of bad bleaching has been owing to insufficient liming, from want of time in the lime. At first it was thought that simply going down into a box about 3 feet deep, up again, and through the squeezers, was sufficient; then an additional box, with three or four rollers, was put before the squeezers; but experience has shown that cloth of average quality does not get lime enough unless it has two or three nips at least, and as many passages through the box, before the last squeeze. In fact, the cloth cannot be too long in the milk of lime; and if the bleacher can spare a washing machine for liming, his work will be all the better; for it must be considered that the cloth going into the lime is saturated with water. It has no desire to take up any more; and all that can be expected is that the milk of lime will displace a portion of the water already in the piece, and take its place. This cannot be done instantly, and cannot be well done in any time that can practically be allowed without the assistance of two or three squeezes of the cloth.

*Amount of Lime to be Used.*—Lime was at first used with great timidity by bleachers, at temperatures far below boiling, and the proportion to the cloth relatively very small. We find indicated in earlier recipes, 1 lb. of lime to 150 of cloth, then 1 to 50, and later, 1 lb. to 35 of cloth; increasing up to 1 lb. of lime to 15 of cloth, which is perhaps the largest proportion which can be profitably employed. Bleachers differ so much in their practice in this respect, that there cannot be said to be any precise rule; but as lime is cheap, and an

excess is not injurious, there are no inducements to keep to a minimum quantity. Whatever be the quantity of lime employed for a boiling—suppose 600 lbs. for 10,000 lbs. of cloth—it is clear that to insure success it must be as evenly as possible divided amongst the cloth. This is secured by keeping the milk of lime in a box at a regulated strength. For practical purposes, the indications of the hydrometer are sufficiently close when observed with some degree of skill. Although this instrument is only intended for showing the specific gravity of actual solutions, it can be profitably employed in several cases of mixtures of suspended matters; but the result must be read off quickly, before the insoluble matters settle down. Though the distribution of the lime over the cloth can be regulated from the box, the only proper way of testing the strength of lime that is going into the kier is by wringing the fluid out of the cloth as this latter is being deposited in the kier.

The use of dilute acids will be found safer as a method of testing and controlling the milk of lime than the hydrometer—commercial muriatic acid reduced to say two degrees of Twaddle, and strongly tinged with litmus; logwood or cochineal answers very well. A stock of this should be kept, and all that is required is a phial marked with a file, at say half or quarter oz. distances from the bottom. Some of the lime liquor either from the box, or wrung out of the piece after leaving the box, is caught in the phial, and a given mark is reached: then the dilute acid is added by degrees, with shaking until the colour shows that the lime is neutralized, and the quantity required will indicate the strength of the lime. The absolute strength of the acid is not important; what the bleacher requires to know is, whether the cloth is getting regularly limed or not with the proportion of lime which experience has shown him to be the best. In a given case, the milk of lime in the box was at 5° Twaddle, and it required rather less than 2 oz. of the muriatic acid at 2° to neutralize 1 oz. of it; the liquor wrung out of the cloth as it was going into the kiers marked about 2° Twaddle, and 3 oz. of it were neutralized by 2 oz. of the acid.

Now it is evident that it requires some care to keep up this or any other ratio between the liquor in the box, and the liquor actually carried away by the cloth, for it is liable to vary on account of the different quantities of water carried into the box by the wet cloth, and by the amount of set upon the pressure rollers. For the latter half of a boiling the lime in the box must be stronger than for the first half: and all through the squeezer rollers must be set so as to allow the cloth to come through tolerably full of liquor, and so wet that a slight wringing causes it to yield the limy liquid in abundance, but not so wet as to cause the draw winces to splash it about the bleachhouse.

*Boiling with the Lime.*—The cloth thus uniformly impregnated with milk of lime is led directly from the liming machine into the boiling vessels, commonly called kiers. Great care is taken to arrange and pack the cloth with regularity: boys lay the long ribband of calico at the bottom of the kier, by means of sticks, and tread down the cloth with their feet until the kier is filled, and it is then run up full with water. The next step varies according to the kind of kier in use; but whichever of the many systems of boiling described further on may be employed, the object is to submit every portion of the cloth to a long-continued boiling heat. The time of heating varies from nine to eighteen hours, and even longer, according to the construction of the kier, the pressure capable of being applied, and the quantity and quality of cloth operated upon. If the boiling in lime has been successfully carried out, a sufficient amount of lime used, and well distributed over the cloth, the heating sufficient and regular and the cloth well laid down in the kier, the most difficult part of the bleaching has been overcome; the cloth, to use a bleacher's phrase, has been well bottomed, and the subsequent operations rendered easy and certain. If, on the other hand, from neglect of any of these conditions of success, the lime boil has not been effective, the after processes cannot correct the error, and if the cloth goes on it will turn out bad. If it is known that something has interfered to prevent full justice from being done to the boil, it is better to lime and boil over again than to try anything else.

When the boiling is completed, it is usual to run the hot liquid off, and fill up the kier with cold water, for it is thought that injury may result to the cloth if left in contact with the heated kier and the lime liquor. Whether this be so or not, it is well to cool the pieces, and then they may be safely left until it is convenient to wash them, for it does not appear that there is any danger of iron rust from the lime kier; however, the bleacher will get them washed as soon as he can, so as to be on the safe side.

*Washing after Liming.*—The pieces are passed through an ordinary washing machine to remove the excess of lime and other removable matters; the cloth may be considered sufficiently washed when the water wrung from it is clear, or it may be tested more exactly by red litmus paper, which changes to blue on contact with lime.

*Souring after Lime.*—The next step is to treat the cloth with a dilute acid. The term "sour" for weak acids, and "souring" for the process of treating cloth with these acids, come to us from the old linen bleaching process, in which the linen was steeped for four or five days in the sour fluids resulting from fermentation of bran or rye meal, or from sour milk, or what was thought best of all, butter milk. Dr. HOME, who paid much attention to linen bleaching in the middle of the last century, has many curious particulars about the souring process, which he considered was principally called for to remove earths, into which a portion of the alkali was changed by continual waterings and dryings of the cloth. Though wrong in this point, he had the sagacity to observe that the mineral acids, especially sulphuric, were quite as effective and much cheaper and cleaner than the sour vegetable and animal liquids then in use. He used "oil of vitriol in the proportion of half an ounce, or at most three

quarters," to a gallon of water, and found the cloth was better with four hours' treatment of these sours than with five days of the old sours; he proved also satisfactorily that vitriol sours, properly used, had no injurious action upon linen; and from this time, and from his recommendations, may be dated the displacement of the old sours. The sours now used are made by mixing either sulphuric acid or muriatic acid with water, and they are applied to the cloth at a strength of from 1° to 2° of Twaddle's hydrometer. As the strong acids are destructive to the cloth, care must be taken that the mixture is properly made; and though it may seem superfluous to say that the strong acid and water should be well stirred together in the mixing cistern, yet serious damage has been known to arise from a neglect of this simple operation.

The mixed acid and water, at a strength double or treble of that required for actual application, may be kept in stone or lead-lined cisterns, from which leaden pipes with gutta-percha stop-cocks communicate with the souring box or souring cisterns. The most modern method of souring is by running the cloth through a machine similar to the lining machine. The pieces pass four or six times into and out of the sours, then between compressing rollers, and are then piled upon a stillage or laid down in a box for three or four hours. The older plan was to steep the cloth in the sours in stone cisterns, and by a pump bring up the liquid from the bottom and distribute it over the pieces. This system was perfectly effective if the cloth was well packed, so that none of it escaped the action of the acid; and the sours could be used for several successive lots of cloth by strengthening up until they got too dirty to be used. The souring machine is, however, an improvement, for the cloth is sure to be uniformly soured if the strength in the box is kept up. There may be a failure in this point if the hydrometer alone is trusted to, because a good deal of lime and other matters come off the cloth, and the liquid may mark 3 or 4 when there is not half a degree of effective acid in it. A solution of caustic soda tinted with litmus or cochineal may be advantageously employed to control the strength of the acid. Caustic soda, about or rather less than 3° Tw., will neutralize an equal bulk of sulphuric acid sours at about 2° Tw. A stock of this may be kept in the bleachhouse, and a small narrow phial, marked with a file at a capacity of 1 oz. from the bottom, and higher up at another ounce, is all the apparatus required. To test the sours the bleacher fills up to the 1 oz. mark with the sours, and then adds the coloured soda until the colour ceases to be changed. Of course the more soda it takes the stronger the sours, and the less the weaker. A skilful bleacher will run his sours rather stronger for the last half of a batch, both because the cloth is wetter as it enters the sours, it loses some sours by draining in the heap, while the lower part of the soured heap gets the drainings, and also because it has the least time in the sour. Of the two acids used for sours there is no doubt that muriatic acid is preferable in a chemical point of view; the compound it forms with lime is extremely soluble, and it has for the same strength a keener action upon insoluble oxides, such as iron and copper, than any other acid. Sulphuric acid is, however, generally used for economical reasons, and it does not in practice present the disadvantages which from theoretical grounds might be predicated. The amount of sulphate of lime formed on the cloth is not considerable; and though it is but sparingly soluble in cold water, it has nearly no attraction for the fibre, and is easily washed off. Souring after lime is not to be looked upon as of absolute necessity, but all bleachers are agreed that it is a very useful step, and contributes powerfully to the regularity of the process. If it is omitted a great deal of dirty stuff goes into the next boil; this could be in great part removed by extra washing instead of souring, but the cost of acid is so trifling, and the additional security so great, that a departure from this process is not to be recommended either on grounds of economy or despatch.

*Washing after Souring.*—This is performed in the ordinary machine, and is simply to remove the acid and all other matters rendered soluble or non-adherent by its action. Of course no sours should be left in the cloth, as they would neutralize the alkali in the following boil, precipitate rosin upon the cloth, and give rise to iron stains by contact with the kier sides before the alkali was run in; and some of these effects are liable to take place if even a very small quantity, inappreciable to the taste, remains in the calico. The cloth should be tested with blue litmus paper.

*Boiling with Soda-ash and Rosin.*—The quantity of soda-ash to be employed will vary, according to the quality of the water and the kind of cloth, from 1 to 3 per cent. of the weight of calico—3 cwts. to 10,000 lbs. of cloth being about the maximum proportion. There are two ways of applying the rosin; the first, to dissolve the crude rosin in the soda-ash just before using; and the second, to dissolve in the solution of soda-ash a previously prepared rosin soap. If the bleacher uses crude rosin the proceeding is as follows:—The requisite quantity of soda-ash is dissolved in an iron cistern, which is provided with a steam-pipe, and which should be placed so high above the kiers that the contents can be run into them by gravitation. The liquid is heated to boiling, and the scum which rises to the top, consisting chiefly of the earthy salts of the water, is removed, and the rosin, broken up, is added. The boiling is continued with stirring until the rosin has been completely dissolved and no particle is visible; this requires several hours; if necessary, the liquid is skimmed again to remove insoluble matters, which if carried on to the cloth might give rise to stains. The quantity of rosin used may amount to one half the weight of the soda-ash, and it is not advisable to exceed that proportion, though any quantity less may be used.

If prepared rosin or rosin soap be employed, the required quantity is simply mixed with the warm solution of soda-ash, and dissolved by heating and

stirring, which take very little time. In this case the proportion of soda-ash is reduced by the amount represented by the alkali in the rosin soap. When the solution of rosin and alkali is prepared it is run upon the cloth, which has been previously closely packed in the kier, and the boiling is proceeded with and carried on for from eight to sixteen hours, according to the quantity of cloth or kind of kier used. When the boiling is terminated, the spent liquid is run off and the cloth washed as soon as possible to avoid iron stains, which are readily formed if the cloth in this state lies for a length of time in contact with the sides of the kier. If the cloth cannot be taken out and washed within a reasonably short time, it is well to leave the liquor in it, and not run off until shortly before it can be moved. The conditions necessary for success in this part of the bleaching process are sufficiency of alkali, and, of course, a proper boiling.

*Washing out of the Soda-ash.*—A single passage through the washing machine should be sufficient to remove all soluble matters; it is important, however, that the cloth should be well washed, and free from rosin especially; for the after processes will have no power to remove it, but rather tend to fix it.

*Treatment with Chloride of Lime or Bleaching Liquor.*—Dry bleaching powder is best dissolved by first making a thick cream of it with lukewarm water, and beating it well together to secure its uniform wetting; for it is rather repellent of water, and if not well mixed at first, small balls form, which are dry in the interior, and interfere with the settling and clearing of the solution. (There is a machine for mixing in use upon the Continent). It may be made to mark from 6° to 8° of TWADDLE's hydrometer, and should form a clear limpid solution, which generally has a sea-green colour in deep vessels. Formerly the goods were treated with the bleaching liquor in large stone cisterns, but in the modern continuous system of bleaching it is applied by a machine similar to that used for liming and souring. The chemicking machine, as it is usually called in Lancashire, is connected with the reservoir of bleaching liquor by leaden pipes, and a sufficient quantity is allowed to run in and mix with the water in the box of the machine, and the strength is kept up by a continual addition of strong liquor. The strength of the solution in the box will vary according to the work from ½° to 1° of TWADDLE's hydrometer, and whatever strength may be decided upon by the bleacher should be carefully maintained for the whole quantity of cloth, due allowance being made for the latter portion of a pile, which coming into the machine wetter than the earlier portion, and remaining less time under its action, requires the bleaching liquor to be a shade stronger. The hydrometer is not a trustworthy guide for dilute solutions; practical men are often guided by their sense of taste, but it is far better to adopt one of the plans of testing given further on, which may be trusted to give exact results. The cloth is left with the bleaching liquor in it for two, three, or four hours, and is then soured; or if time permits it is washed before souring, by which the unchanged chloride of lime is in great part removed, to the great convenience of the hands employed in souring.

*Souring after Chloride of Lime.*—This souring is conducted in the same manner as the souring after lime; but as, in nearly all cases, there is liberation of chlorine gas, the souring machine should be provided with a hopper and tube to carry the greater portion of it away. The soured goods themselves will sometimes smell so strongly as to seriously inconvenience the boys engaged in laying them down. There can be no doubt that, in such a case, there has been too much bleaching liquor used, probably to cover a fault in one of the boilings; or else the cloth has not lain long enough in the bleaching liquor before souring. This last souring is important, and must be carefully attended to; the strength of the sours must be kept up, so that no part of the cloth is undersoured; and it is clear that the other extreme of oversouring must be carefully avoided, or there will be difficulty in washing the sours out. The sours both in the box of the souring machine, and as they are expelled by wringing the cloth, should be tested at frequent intervals by the alkaline test liquor. A strength of 1° to 2° TWADDLE in the box, and of 1° to 1½° in the cloth, is about right for regular printing cloth. The cloth is left with the sours in for not less than an hour, and longer if convenient.

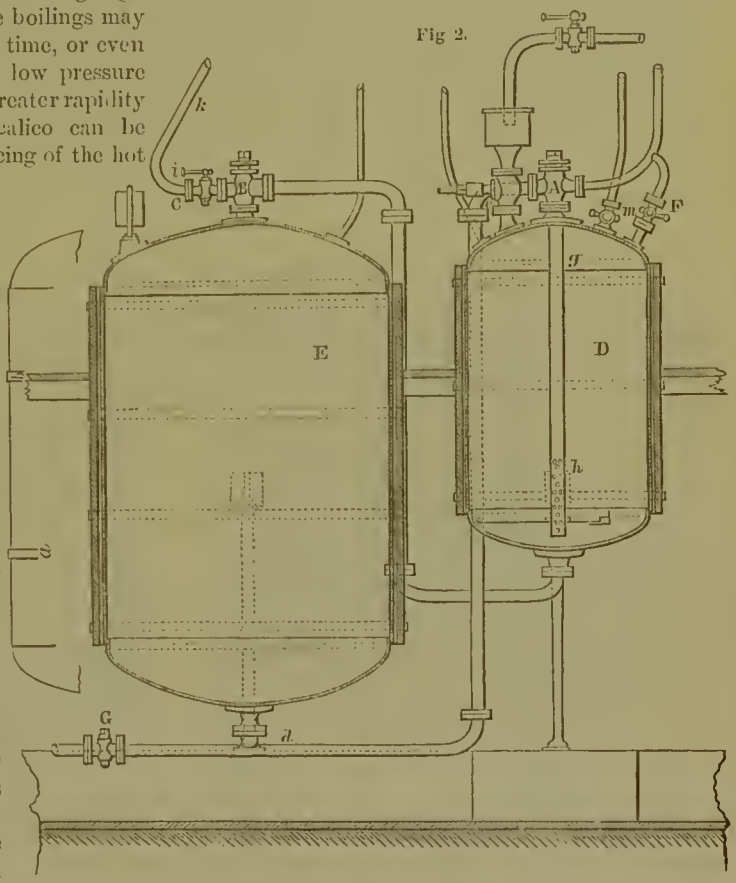
*Final Washing out of Sours.*—All that is required in this washing is that there shall not remain any trace of the sours in the cloth: and the bleacher ought to ascertain from time to time that this is the case by testing the cloth with blue litmus paper; and if there is the least uncertainty about it, the cloth should be rewashed. With a good supply of water, and ordinary care that the cloth is not too tight, one passage in the washing machine is sufficient. The calico now only requires squeezing and drying. The squeezers should have a water box fitted up in front, say 3 feet long, and furnished with rollers above and below, so that the cloth may have the advantage of a final rinse before it goes to the drying machine. Warm water is sometimes used in this box, and warm condensed water has been recommended as softening the cloth. If the condensed water is free from grease and iron, no doubt it is a good thing; but experience shows it to be a risky refinement, on account of probable impurities from the boiler or pipes.

*High and Low Pressure Bleaching and Working of Kiers.*—Although there are sufficient indications that high pressure, or the employment of temperatures higher than could be obtained by boiling in open vessels, was aimed at and actually used by CHAPTAL and others in the last century, the process was not put into a practical form until about twenty years ago by PENDLEBURY and BARLOW. Up to that time boiling was all done by low pressure steam, and the kiers were either quite uncovered or only lightly closed. At the present time the high pressure system is preferred, as being more rapid and economical, and its use is spreading; but there are still

many and important works where the low pressure kiers are in use, and where the souring and chloring are performed in sunk boxes or pits. In point of quality there is no difference. One system of bleaching is as good as the other; and the low pressure bleachers express their belief that the cloth is less harassed, and not less perfectly bottomed, by their system than by high pressure. The frightful accidents which have resulted from the explosion of high pressure kiers had the effect of causing managers for a time to reduce the working pressure from 50 lbs. per square inch to 30 or 35 lbs. The writer has no hesitation in saying, that if the kiers must not be worked at any greater pressure than 30 lbs., there is no great advantage in having high pressure arrangements. At 50 lbs. the boilings may be effected in about two-thirds of the time, or even in one-half of the time, necessary for low pressure boiling, and this chiefly owing to the greater rapidity with which the mass of cold wet calico can be heated to the boiling point by the forcing of the hot fluids and steam through it; whereas in the low pressure kiers the steam is turned on several hours before the mere gravitation of the heated liquid falling from the throw-up pipe causes it to effectually percolate and influence the bulk of the cloth.

Fig. 2 shows one modification of PENDLEBURY'S high pressure system; the cut and description of the method of working are taken from an excellent paper of M. EMILE BURNAT, in the thirty-eighth volume of the *Bulletin de la Société Industrielle de Mulhouse*, which shows the method of working at the great calico printing works of DOLLFUS-MIEGS. The cloth kier, E, is about 13 feet high and 6½ feet in diameter, and will hold about 8000 lbs. weight of calico. The liquor kier, D, is about 8½ feet high and about 4¾ feet in diameter, and holds from 900 to 1000 gals. of liquid. The cloth is "entered" and the man-holes secured, and it was the custom to commence by blowing steam through the cloth until it escaped at G. This took twenty minutes, and the pressure on the upper part of the kier indicated from 20 to 30 lbs. The object of this blowing through was to heat the cloth and expel air; but it has led to frequent accidents in tossing about the cloth, and it is now usually dispensed with. The liquor kier, D, filled with water and soda up to *g*, is now heated by the steam from A, which passes to the bottom of the kier through the pipe *h*; the liquor is then forced into the cloth by shutting the tap A, and opening the taps F and B. This is a departure from the original method of working which was found advantageous. It takes about twenty minutes to pass the liquid over the first time, and then the pressure in E will be found about 52 lbs., and the pressure in D about 60 lbs. The valve, F, is now closed, and C and B are opened, so as to raise the pressure in E somewhat higher than in D (it is sometimes necessary to open the waste-pipe, *m*, to relieve D, but not usually). When this is accomplished, B and C are shut, and A is opened, the effect of which is to put E into connection with D by means of the pipe, *d c*, going from the bottom of E. The liquid being cooled by the cloth in E, enters D slowly at first, but condensing, the steam forms a vacuum which speedily draws the whole liquid contents of E over. The liquor is again heated by steam coming through A; and when the pressure is up, it is driven over into E by a repetition of the first process, and so on until the cloth gets so hot that the liquor coming into D does not form any

Fig 2.



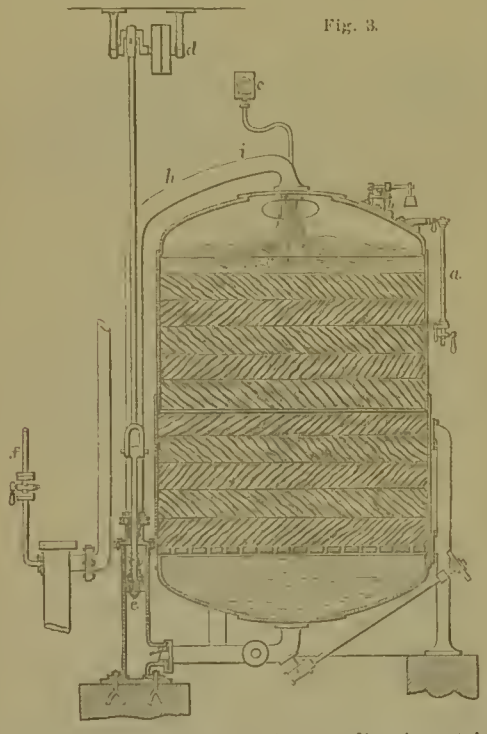

suitable rarefaction; and then the tap F is not further used, but the whole managed by the three-way tap, A. An expert workman can drive the liquor in and out of D six times in an hour. When the boiling has been sufficiently protracted, the let-off tap G is opened, and the liquor driven out; the man-hole covers removed, and the cloth taken out as soon as it is cool enough to handle.

Many varieties of kiers have been introduced, but none others than those mentioned have been largely used in practice. Attempts, more or less successful, have been made to work single kiers upon a circulating principle; some by naked fire, others by allowing a blow-off in the upper part of the kier, and others by employing pumps. Fig. 3 shows the arrangement of one of the latter class.

It is a kier patented by M. Scheffer-Rott, of Thann. It requires no explanation but to state that the liquor is heated by the steam from *f* as it passes from the pump, *e*, by means of *h i*, to the top of the kier. *a* is the water gauge, *b* a safety valve, *c* a pressure gauge, *d* the pump crank, and *g* the let-off tap. It is said that this kier works well with soda, but that with lime the top pieces become tender.

In Barlow's kiers, when boiling with lime, a departure from the usual routine has been advantageously adopted. Both kiers are run up with water to a sufficient depth, and for a couple of hours the taps charged every five minutes, and then every twenty minutes to the end. This never leaves the cloth in the kier dry, and has proved in some places a remedy for stains of very uncertain origin. A drawing and description of Barlow's kiers is given in article Bleaching, pp. 372, 373.

Fig. 3.




Shearing.—The surface of the calico is not in a fit state for good printing as it is received from the bleachhouse; upon close inspection it will be seen that there are projecting knots and floating threads which could not be expected to be removed by the rapid and momentary process of singeing; there are also abundance of fibres, coarser than the hairs taken off by singeing, all of which together would be a hindrance in printing, accumulating in the colour box and giving rise to bad cleaning, or remaining on the cloth only to be detached or moved in the subsequent operations, and leaving unsightly white specks where there should be an even colour. Until lately these accidental obstructions were removed by drawing the whole calico, yard by yard, over a flat table, and cutting them off with sharp scissors by hand. About 1840 the shearing machine was introduced into calico printing: it is believed from America. A similar machine had been for a long time used in dressing woollen cloth, and but few changes were required to adapt it to calico. At first it was proposed as a complete substitute for singeing, but it was found that for high-class printing it was extremely defective, and it was some years before it found its proper place in the business. All the various makes of shearing machines are constructed upon the same principle; a shaft of the width of the piece carries a number of steel blades with serrated edges; these blades are fixed spirally on the shaft, and are ground to a very true cylindrical shape. This shaft is driven at high speed in close proximity to a stout steel "doctor" firmly fixed in the framing of the machine. The cloth is made to travel in a state of tension over the blunt edge of the doctor and between it and the rapidly revolving cutters; the doctor-blade is so set that the cutters just escape the true surface of the cloth, but intercept, cut, and remove all projecting matters. When the cutters are in good order they not only remove gross and bulky substances, like threads and knots, but a great deal of downy, fluffy matter, especially from calico made from short staple cotton; and it is certain that this fluffy stuff, if it were not taken off here, would make its appearance in the colour or on the lint-doctor of the printing machine.

In shearing calico made from East Indian or other Asiatic cotton, so much matter is detached by the shearing that the atmosphere of the locality is filled with downy particles; and unless some effective system of ventilation exists by which they are removed, some portion settles down upon the cloth and gives trouble afterwards in the machine room. Those only who have been compelled to work where ventilation was impracticable, and the shearing machine placed near the printing, can understand all the difficulty arising from this circumstance. All good shearing machines are boxed in their lower part, and have receptacles to retain the matters cut off, but only a few have a connection with an exhaust fan, which at once removes all chance of injury from fluff.

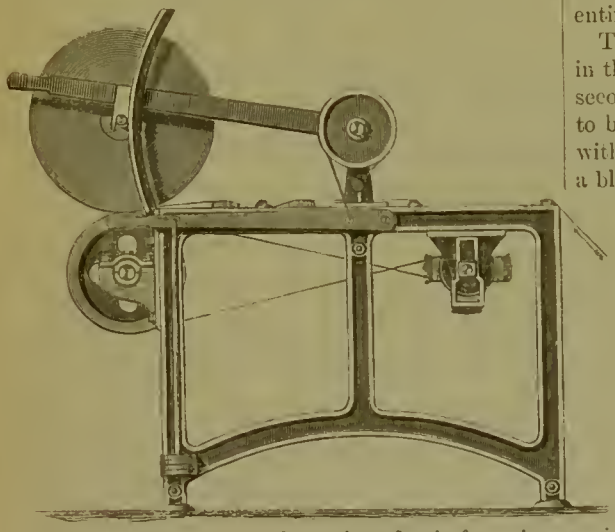
Winding-on for Printing.—This is a simple process which is sometimes performed with the shearing, but is usually a separate operation, and is combined with a further cleansing of the cloth. The object is to wind the calico upon a roll for the printing machine. It should be done with an even and steady tension, and the selvedges carefully guided. The winding-on "canroy" is usually fitted with a circular brush to catch loose threads or other matters, and sometimes in foreign machines supplied with a set of beating rods, to shake dust out of the cloth.

Fig. 4 shows the most modern form of the canroy. The cloth enters on the right in the direction of the arrow; the roller with brushes revolves against the travelling cloth, which passes over stretching and scrimp bars, and is wound on a proper roller. The pressure upon the roller is regulated by the tension of a band passing in a circular groove of the arm fixed on the framework of the machine, the other

end of which bears upon the metal axis of the roller or shell. A curved guide keeps the centres of the driving drum and roll of cloth perpendicular to one another.

Of the other treatments of cloth previous to printing little need be said, as they are exceptional. For fitting stripes another system of winding-on is required; for printing check patterns the cloth is better for being prepared in a stenting frame, by which it is made "square," that is, all the weft threads are made to take a position at right angles to the warp threads, as when they left the loom, but which in many cases is materially changed by the irregular and violent tension in modern bleaching processes. Those preparations of the cloth which consist in impregnating it with solutions of salts or mordants, are treated of either in connection with particular styles or in the section on mordants and prepares. The conditioning of calico for printing by mechanical means is difficult and impracticable for the most part. Cotton has so great an avidity

Fig. 4.



for moisture that a very short time fits it for printing, even if it has been excessively over-dried; but it is very desirable that the "white room" should be in a cool locality, and that there should be always twenty-four hours' stock of cloth in it. It is far better for the cloth to be over-dry than the least moist, for in the latter case it takes off the plane parts of the roller that small trace of colour which is left on by the doctor, and the whites show it, to the great injury and even complete spoiling of the print in certain colours.

Application of the Design to the Calico.—It is probable that this was done at first by brush or pencil. It is recorded of the celebrated French house of Kœchlin Frères that, when they first commenced operations as calico printers (1746), all their goods were done by pencilling. The pencil, to fill in certain colours, was extensively employed both in France and England at the end of the last century in the best quality of prints; it was employed in England within the memory of living printers, but at the present time it is not used in any part of Europe; the name "pencil" remains attached to one colour, which could only be successfully applied by pencil, the orpiment solution of indigo, which both in French and English is called "pencil blue."

The use of blocks probably next followed; when introduced it is impossible to say. Mr. Merrifield concludes that blocks were not known in England at the date of the MSS. of Jehan de Begne, 1410, but it is probable their use in calico printing preceded their application in book printing.

In modern calico printing the block-printer fills a very subsidiary position; 99 per cent. of current prints are never touched by block, and of the remainder the block printer is only required to enter some colours which cannot be conveniently printed along with the main elements of the design. In some branches of woollen printing, and especially with heavy goods, as table-covers, carpets, and the like, all the printing is still done by block, and in some parts of the Continent, where labour is cheap and machinery dear, certain qualities of ordinary calico prints, in five or six colours, are worked entirely by block.

The apparatus of the block-printer consists first in the block upon which the design is cut in relief; secondly, of the sieve which contains the colour to be printed; and thirdly, of a strongly made table with a smooth surface of wood or stone covered with a blanket.

The block is variously made; for objects of moderate thickness and simple arrangement the design is cut upon some close and tough-grained wood like pear tree wood; for blotch or thick objects, the outline only is cut on the wood, and the inner part is hollowed out, and filled with fine cloth or felt called batting. In order to prevent the warping of the block by successive wettings and dryings, it is backed by one or two layers of wood, fixed with the grain in a different direction, generally at right angles to the grain of the cut part. For finer lines or prints the wood is too fragile, and they are formed by copper wire flattened or drawn to the proper shape, and imbedded in the wood. Very elaborate and costly blocks are made entirely of such copper wire embedded in the wood. A more economical method of attaining the same end is by a modification of the stereotype process in letterpress printing; a mould is made by cutting or burning in a block of wood, and a fusible alloy run into it; this produces a casting, which is fixed upon a wooden block, and which being trimmed and smoothed, gives an accurate and durable printing surface.

The sieve, so called from its external resemblance to that article, is usually a round shallow wooden vessel, inside of which fits loosely a wooden hoop, covered with a waterproof cloth, and like a tambourine; the outer vessel or tub is partly filled with a pasty or gummy liquid, usually old or spoiled colour, and the waterproof tambourine swims on this pasty mass. A piece of fine woollen cloth free from nap is placed on the bottom of the tambourine, and

the colour to be printed is spread by means of a brush on this cloth in an even and regular layer. The block with the cut part downwards is lightly pressed on this layer of colour; it takes up a portion, which is then transferred to the cloth to be printed.

It will easily be understood that a yielding, elastic surface, such as is obtained by this contrivance, is very suitable for imparting colour to all patterns of the block which stand in relief, and it is the invention of the sieve which enables very excellent effects to be produced by block-printing. The Chinese of this day are described as using blocks for printing calico, but not knowing or not using the sieve, their process is exceedingly slow and laborious.

All the contrivances to print more than one colour by one impression of the block, which have met with any success, are based upon modifications of the sieve. There are many methods of so arranging the sieve that one part of it shall be supplied with one colour, and another part with another colour, to the number of six or eight; and if the block is cut and guided to press only upon these parts, it takes up the colours without confusing or mixing them, and they can be transferred to the cloth. One of the most usual apparatus is generally known in the trade as the "Toby Tub." The sieve cloth in this case is of an open texture, and cemented to the borders of a series of canals cut in wood which supply the colours from beneath. These canals, of which there are as many as there are separate colours, are so led under the sieve cloth as to come to the surface in the proper places for the pattern cut on the block, and keep these places moist with the respective colours. The reservoir of colour is usually an inverted bottle acting as a fountain, and keeping the supply always at the same level at the heads of the canals. In "peg printing" with several colours at once, the colour is furnished to an ordinary sieve by means of a sort of rough block with projecting pegs; these pegs dip into vessels of colour, and furnish the sieve from which the block-printer supplies his block.

No fine printing can be done by any of these arrangements, and they are restricted to putting on solid objects mostly within boundages, and where exact outline is not necessary.

The block-printer's table requires little description; for regular work it is about 6 feet long, but for special purposes there are tables 30 feet or more in length, so that the whole of a piece can be put into position at once. The attempts which have been made to apply machinery to block-printing have not been productive of anything permanently useful to the trade of the garment printer. The machine which has been most widely employed is that called the "Perrotine," but though a few of these machines are still in work on the Continent, it is doubtful if one has been in use in Great Britain for many years past. The variety of block-printing called surface printing, and consisting of a number of blocks fixed upon a cylinder, and supplied with colour by an endless sieve cloth, has almost entirely disappeared from regular calico printing. The great advance which has been made in the art of engraving copper rollers has made it possible to produce effects by their means, which a few years ago could only be accomplished by block or surface roller.

Stencil plate printing was formerly practised, as is evidenced by Elliot's patent in 1751, Nicholson's patent, 1790, and others; the latest patent referring to this method of printing is to Henry (communicated from Despreaux), 5th December, 1861; but it is only a very exceptional process.

Roller or Cylinder Printing.—The earliest description of a roller printing machine is contained in a patent to Keen & Platt, 10th March, 1743; it describes a machine for printing three colours, a separate bowl to each colour. A single roller printing machine was patented in 1772 by Atkin; the printing roller was made of sycamore, and engraved to the depth of $\frac{1}{8}$ of an inch. It occupied the middle place between two other rollers, running in slots in upright oaken beams; the lower roller furnished the colour, and the upper roller acted as the bowl—how the roller was cleaned from excess of colour does not appear. The machine was driven by power applied to the projecting axis of the middle roller. Whether this and similar machines were ever practically used in the trade is uncertain, but it is clear that the idea of continuous printing from circular surfaces was abroad; and as at this date the engraving of flat copper plates, and printing from them, was carried to a high degree of perfection, the time was come for a radical change in the system of calico printing. The credit of inventing the printing machine, essentially as we have it now, is generally ascribed to Thomas Bell,* whose first patent is dated 17th July, 1783. He figures and describes a cylinder machine for printing six colours at once. In all the first machines the rollers were arranged in a manner which seemed quite natural to the inventors, but very curious to modern printers—upon the upper part of the bowl or cylinder. In Bell's second patent, 9th July, 1784, he describes a three-colour printing machine of the same general construction as the six-colour machine of the previous year. In these patents occur the first mention of "doctors" and "box-doctors" for furnishing colour, of scrimp rails, iron mandrills, and copper shells. In Slater's patent, 29th April, 1784, for a surface printing machine, lapping is first mentioned for the bowl and for the furnishing rollers; brush furnishers are also mentioned. In Paul's patent, 1796, there occurs the first mention of box wheels, mandrills with turned necks to work in steps, and made square in the body to prevent the turning inside the roller; also a traverse motion for the tearing brushes. It seems certain that Bell's machine was applied at Livesey, Hargreaves, & Co.'s works, near Preston, in the year 1785, and was really the first machine known to work satisfactorily. Bell may be considered the inventor of the printing machine in the same sense that Watt was the inventor of the steam engine. They each

* The claims which were formerly made in favour of Oberkampf, a French printer of the last century, are now quite withdrawn by all respectable authorities; although it still continues, probably from oversight, to be inserted in late editions of Girardin's Leçons de Chimie

found something before them, very clumsy and ineffective, and by their discoveries made it practical and efficient.

Plate I. shows the sectional elevation of a modern machine capable of printing designs of twelve colours, or any less number; the Plate shows it fitted with rollers and colour boxes for the whole twelve colours. The calico proceeding from A, in the white state, is delivered at L, imprinted by each of the twelve rollers with the portion of the design proper to each roller, and with the shade of colour required to obtain the effect intended. The necessary pressure for printing is obtained by means of screws and levers; and in the case of the former there is to each nut through which the screw passes a backing of stout india-rubber rings, which gives a certain amount of elasticity, and avoids the inconvenience which would result from irregularity in the thickness of the blanket acting upon a fixed unyielding pressure. The back grey is not seen entering the machine. At the exit the letters, M N, should be transposed, the back grey being next to the printed piece. The references engraved on the Plate will explain fully the other details of this machine.

Plate II. shows a printing machine for eight colours, by the same makers, in front view, and the method of driving it by an independent engine. Printing machines, especially when exceeding eight colours, are best driven by separate engines, on account of the control which the printer has over the speed at which it is desirable to print, and the ease and smoothness with which the machine can be stopped and started. But separate engines are of comparatively modern introduction in machine printing, and the greater number of machines are still driven by main-shaft and cogged gearing from the principal engine of the print works. By an arrangement of different sized cog-wheels and levers for connecting them with the shaft, the printer has command of three different speeds, slow, medium, and quick; but the starting of the machine and changing of the speeds while at work are accompanied by jerks and shocks of a disagreeable kind, often giving rise to accidents. Many attempts have been made to remedy this inconvenience by the adaptation of friction gearing, but it is believed that none of the systems in use answer in a satisfactory manner. The continental machines, which are not provided with separate engines, are for the most part driven by broad straps and pullies, and this would seem the best method of driving by friction, for though expensive, and requiring much attention, the starting, stopping, and driving are very smooth, and without shocks.

The waste or exhaust steam from the small engines can be utilized for heating the drying apparatus attached to the machine. The drying apparatus consists of a number of hollow cast-iron chests supported on an iron frame. They are heated by steam, and the printed piece is made to pass close to, but not in contact with, the heated metal. The speed of printing depends in a great measure upon the power of the drying chests, for it is an essential point that the colour shall be quite dried upon the cloth before it leaves the machine. To secure sufficient heating surface the steam chests are multiplied to the number of fifty or sixty, and the printed piece, as well as the blanket and back grey, led by means of rollers up and down among the heated chests, so as to utilize as much as possible of their heat.

Plate III. shows an elevation of a twenty-colour machine made by Gadd of Manchester. It is the largest machine which has yet been constructed, and is now working at the Castleton Print Works, near Manchester. There are very few styles in which more than a dozen colours can be effectively combined; but this machine, as well as machines for sixteen colours, are regularly in use for printing elaborate furnitures and hangings, which imitate very well at a very low price the costly productions of block-printing. Although this machine has been called the largest machine yet made, this must be understood only of the number of colours which can be printed. There was a machine made some years ago by the same makers for printing only three colours, but as the printing rollers were to be each 5 feet in diameter, instead of 6 or 8 inches as in the usual machines, the framework and bowl would make it the largest printing machine in existence. It was believed to be applied to the printing of imitation Indian shawls. What success attended its application, or whether it is still at work, the writer has no knowledge.

Plates IV. and V. illustrate the most modern make of a French printing machine for printing eight colours, constructed by MM. Tulpin Frères, of Rouen. Plate IV. gives a front view and shows the method of driving. The most noticeable feature in this is that the box-wheels, instead of being on the mandrills, are separated by shafts of 3 feet or so in length, which carry conplings to connect the mandrills. This construction is believed by continental makers to give a truer motion to the rollers and to require less power, diminishing or destroying, by means of the two bearings in the intermediate frame, the twist produced by the action of the cog wheels upon the roller in the usual English construction. Further, it will be seen that the main bowl is movable, and intended to be raised entirely away from the rollers by means of the fly wheel, F, acting upon the screw, H (Plate V.). This arrangement is not found in any English machines of modern construction. It apparently facilitates the labours of the printer when changing rollers and cleaning up; and when the machine is stopped for half an hour or so, without requiring to change rollers or colours, the bowl is raised and the rollers slowly driven, which perhaps may save some trouble at re-starting, by preventing the drying of the colour on the rollers. In Plate V. it will be seen that all the rollers have a lever pressure, most of them of a direct simple action; and further, that the printer is able to command the four rollers at the back of the machine without stirring from his place at the front. Other details are sufficiently explained by references on the Plates.

Such is the printing machine supplied at the present day to calico printers. Its construction varies in details as made by different houses, but not in any important particular; and now it remains to consider the appurtenances which are necessary for printing, and the application and management of which constitute the business of a practical machine printer.

*Lapping.*—The bowl is first to be lapped with several folds of cloth, in order to obtain a surface with a certain amount of compressibility and elasticity. The ordinary lapping is a strong and rather coarse tissue made with a woollen weft and linen warp. There are various qualities of it, differing in fineness according to the style of print required; but in all the qualities it should be made of very good materials, for it has not only to resist enormous pressure, but also a pulling and grinding motion which speedily destroys inferior materials. The first layer is made to adhere to the bowl with gum or paste, and the additional layers smoothly and tightly wrapped round; the ridge which would be left on the last round is softened and reduced by drawing out 2 or 3 inches of the weft threads, and laying the warp threads smoothly down on the previous layer. The thickness of lapping to be applied depends entirely upon the nature of the goods and kinds of colours to be printed, and is a practical detail to be left to the discretion of the printer.

Besides the ordinary lapping, there are lappings made of calico and other materials, coated on one side with solution of iudia-rubber and gutta percha; these have been very profitably applied in many places, but cannot be said to be in general use, on account of some practical difficulties connected with changes which take place in the india-rubber by pressure and heat.

It has been proposed to cover the bowl with a fixed layer of gutta percha, and endless sack lappings of elastic cloth have been made, which had to be slipped over the end of the bowl, requiring the side of the machine to be taken down; but these contrivances have only a limited application.

*The Blanket.*—This stands in the place of the table blanket of the block-printer. It is a fine, thick, strong woollen cloth, made from very good wool, and woven in lengths of 40 or 50 yards; it is of various widths and fineness, and may cost from 9*s.* to 12*s.* per yard; it is fitted on the machine so as to run endless, and the extremities are joined by careful drawing together with fine woollen or silk thread.

The Mackintosh blanket was introduced in 1840 by Leese. It consists of three or four layers of calico cemented together by solution of india-rubber. It is much employed in machine-printing, and preferred to the woollen blanket for some styles, especially for working with fine and therefore shallow engraving. It is not so soft as the woollen blanket, and is not so suitable for deep engravings, for printing massive objects, or generally when it is required to transfer as much colour as possible from the engraving to the cloth.

Blankets made entirely of cotton have also been introduced from America, but though said to be applied there with success and economy, have not found much favour in this country.

The blanket is the true printing surface, upon which the cloth rests when it is receiving the impression; but it is found highly convenient to interpose a piece of calico between the blanket and the piece to be printed. The principal reason for this is to preserve the very expensive blanket from being soiled by the colour, which often passes right through the printed piece, and also from the colour on the extreme ends of the roller, which cannot be always cleared off by the doctor. Unbleached calico is usually employed for this purpose, and the piece is generally known as the *back-grey*. The same pieces may be used two or three times, and are then sent to be bleached and afterwards printed as white calico.

Blankets can be entirely dispensed with by using two or three thicknesses of grey cloth; and many machines are fitted up with what is called grey tackle, by means of which the same length of grey cloth going from a roll is made to pass in a double or triple fold between the lapping and the white piece. This system, which promised to relieve printers from the expense of blankets, is not found, however, to be of such general application as was at first predicted, principally on account of the large stock of greys which would be required, and the inevitable though small damage to the greys themselves.

*Washing of Blankets.*—The blanket in course of working gets incrusted with colour near the edges, which must be removed from it at certain intervals, necessitating the running of the machines for two or three hours while it is washed and scraped, or else the taking the blanket out of the machine. To avoid this some machines are fitted up with blanket-washing apparatus, which is in continual action. Dalglish's method includes a squirt pipe, with brushes and a scraper; a revolving sponge serves to absorb the water. There are other methods similar; but the inconveniences attending the use of such apparatus is so great that they are of very limited application, and do not seem to be required, except in working many-coloured patterns in steam colours upon delaines or woollens, where the engraving is very strong, and much colour passes through the piece.

*Mandrills and Rollers.*—The mandrill is a shaft of wrought iron or steel made to fit the copper shell which bears the engraving. It is provided with a slot to fit a corresponding tab in the interior of the shell, so as to prevent any turning of the one inside the other. The ends of the mandrill are turned to fit the brass steps which carry it, and it is connected with the driving wheel of the machine by a complex cogged wheel called a box wheel, which fits on the end of the mandrill, and is secured on it by a cotter. The attempts which have been made to construct adjustable mandrills have not had much practical result; the parts have not sufficient strength to resist the usual rough treatment of a printing-room, and little change has been made in the mandrill from the

commencement of cylinder printing. Steel mandrills are more rigid than wrought iron, and less liable to yield under the pressure brought to bear in printing; but they are, on the other hand, more brittle, and have been often seen to give way and break at the shoulder, near the step.

The copper roller, which is engraved with the design to be printed, is a hollow cylinder having a thickness of copper varying from 1½ inch to less than ½ inch. Engraved copper cylinders are mentioned in a patent granted to Fryer in 1764, twenty years previous to Bell's patent for the cylinder printing machine; but it is believed that all the copper cylinders used at that time, and long afterwards, were merely plates of copper bent round a mandrill, and the edges secured by soldering or brazing. The production of rollers from solid ingots of copper by drawing and boring seems to date from 1811, the process being described in Fothergill's patent of that year. Many efforts have been made to make use of thin copper shells instead of the heavy and costly roller; but unless used with a permanent mandrill, and very well secured to that, they get speedily injured in working. Covering iron or cheap metals with a coating of copper, by electricity or other means, has also been attempted, but as yet without any practically useful results. Brass rollers are employed to a limited extent; but the metal is never so compact and homogeneous as copper, and presents difficulties both in engraving and printing.

*Engraving.*—The engraving of rollers is sometimes carried on in the print works, but more generally outside, by special engraving establishments. It is an art of itself, which, with copper roller making, is carried to the highest degree of excellence in Great Britain. In every print-works there should be means of repairing damaged engraving, polishing rollers, touching up defective parts, and deepening where the engraving has become too shallow. Only a brief and elementary account of the methods employed in engraving for calico printing can be attempted here.

Engraving by hand by burning is now extremely limited. It is only used in designs of very large sketch, such as for hangings, furniture, and shawls.

Mill engraving is employed for designs of small sketch—that is, where the same object or figure is repeated at short distances in the design. The figure to be engraved is cut by hand upon a small cylinder of softened steel. When completed, the metal is hardened, and an impression in relief is obtained from it upon another cylinder of soft steel by a very powerful rolling pressure. This cylinder being somewhat hardened, is the mill, and is used to produce the engraving upon the comparatively soft copper by pressure in a specially constructed machine, in which the roller to be engraved is made to receive the impression all over, or in certain parts only.

Engraving by etching with acids was practised at very distant periods for fine art purposes, but was not largely used for calico printing until after the discovery of the Pentagraph machine. The system of engraving by etching consists in covering the plain copper roller with a layer of bituminous varnish, capable of resisting for some time at least the action of strong nitric acid. The varnish is removed by a sharp pointed instrument in every place where the design requires it. The roller is then placed in a bath of nitric acid, which etches or eats into the bared metal to a depth sufficient to carry colour. It is then washed, the varnish removed, and with some little polishing is fit for the printer.

The Pentagraph is a machine for quickly and accurately moving the sharp points which cut the design through the varnish; and where diamond points are used, the surface of the copper itself is slightly abraded at the same time, and the commencement of the etching action very much facilitated. This most ingenious and valuable machine could not be described without detailed drawings. By it an unskilled hand, by causing a tracing point to follow an enlarged drawing of the design upon a metal plate, makes diamond points, varying from six to forty-eight in number, simultaneously to move and cut through the varnish on the roller in the most regular and exact manner, reproducing on a diminished scale the drawing traced over. It is only necessary further to mention that punches, ruling machines, and electrical deposition of copper, are also employed in producing engraved effects on rollers.

*Doctors.*—The doctor blade used for scraping the excess of colour from the roller is usually made of steel. It may be from a sixteenth to the twenty-fourth of an inch in thickness, 2 to 3 inches broad, and somewhat longer than the length of the roller. It is very uniform in thickness and in quality of metal, finely tempered enough to take a keen edge, but not so hard as to be difficult to cut with a good file. It is supported by being screwed, for all its length and ½ inch of its depth, between two plates of iron, usually called the doctor shears, which have bearings at the ends to fit in steps, and are also provided with means of connection with the traverse motion.

Composition doctors are made of brass, and are used for some colours which act rapidly upon steel. The so-called silver-nickel doctors are supposed to be still less easily acted upon than composition doctors. Neither of these can be tempered to so exact a degree as steel. They are always soft, do not wear well, and do not clean so reliably.

If there is one point more than another about a printing machine which tests the skill of the printer, it is shown in his knowledge of the management of the doctor. Well used, it produces clean work, full impressions, and preserves the engraving; unskilfully employed, the prints show streaks and smears, the impression is bare and uneven by the colour being dragged out of the engraving, and the engraving becomes so torn up and worn out as to be unfit to print in a very short time. The whetting of the doctor, the nature of the edge to be put on, the angle at which it is to be applied to the roller, the weight to be hung on the shears to keep it in

contact with the roller, the thickness of the doctor blade, and other like points, are only to be learned by experience and observation, since they must vary for different styles of engraving, thickness of colour, and style of work.

The traverse motion of the doctor is obtained in various ways, and very important improvements have been made in it of late years. In the older machines the traverse was obtained from the blanket roller, and consisted in a simple backward and forward movement of a fixed and unchangeable range; in the modern machines the traverse is a very complicated movement, though obtained by simple means, and is so managed that any given points of the doctor and roller fall in the same line only at considerable intervals. The effect is, that the wearing of the doctor edge is made much more uniform, and the destructive action upon the engraving is reduced to a minimum amount.

*Fitting of Patterns.*—When designs of two or more colours are to be printed the question of fitting comes into consideration; that is, the placing and keeping the different rollers in positions so that the parts of the design fall accurately in their right places. Supposing the engraving to have been well done, the following are the principal means at the disposal of the printer for fitting. Marks called pitch-points are usually made near the ends of the rollers at first; the rollers to be fitted being placed in the machine, the printer roughly fixes them so that the mark made by the pitch-point on the first roller falls as near as may be on that made by the second roller, and so on for the remaining rollers; and then the box-wheels being fixed on and geared, the adjustment is completed by the box-wheel, which enables the printer to turn the roller and mandrill to a limited extent forward or backwards in relation to the direction in which the piece travels. To obtain a change of lateral position the steps carrying the mandrill are made movable, and by a screw the mandrill can be forced to the right or left as required, and a further range can be obtained by raising or dropping the steps, but good printers very rarely use this means, except to a very limited extent. Notwithstanding all the care and accuracy which are spent upon the machine, it is evident that the lapping, blanket, or even the bowl itself, and the driving wheels, can only be approximately true; and as in some close-fitting patterns a hair's-breadth out of truth spoils the work, the printer cannot leave his machine for a minute when it is printing, but with the screw-key in his hand watches closely the progress of the piece, and is incessantly moving about, backwarding this roller, forwarding the other, moving this slightly to the right and the other to the left, raising one end a little and dropping another, thus counteracting the inequalities and inevitable defects of the machine, blanket, and cloth. The engraver does all that is possible to make the fitting easy, and takes advantage of all the points in the design where any overlap can be allowed, or where one colour can fall without injury upon another; an allowance is made for the stretching and narrowing which the calico undergoes by the tension it is subjected to between the first and second rollers, and even beyond that. It is plain that the calico must enter the machine at a constant state of tightness; this is attended to by having it carefully wound on beams, and fed into the machine well stretched by means of scrimp rails and friction bars; and this duty occupies the whole time of an assistant, whose place being at the back of the machine, is generally called the back-tenter.

Colour Mixing for Printing.—The mechanical operations in the colour shop will vary in different places, but they may be said to consist in mixing, boiling, and straining the colours. It is not intended in this part to enter into details of particular colours, but in addition to the routine practical operations, it will be necessary to study the general character of thickeners, vehicles, and mordants.

Fig. 5.

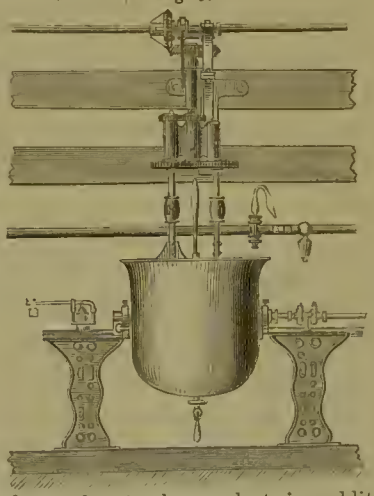
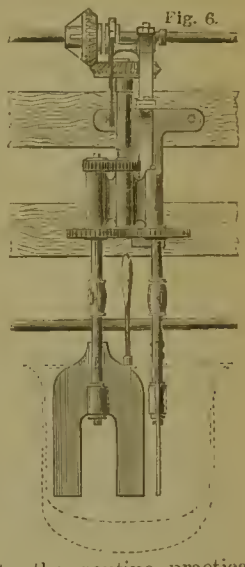


Fig. 6.



*Boiling Apparatus.*—Most of the materials for making colours are supplied to the colour-mixer in the liquid state, or he finds it desirable to dissolve them himself; and to bring them to a suitable consistency for printing they must be incorporated with some thickening matter, which is usually performed by heat. The pans of a colour shop are made of copper, double cased, and heated by steam; other modes of boiling are quite exceptional. The modern colour shop range consists of a number of these double-cased pans of various sizes, fixed in a cast-iron frame and connected with steam pipes for heating, water pipes for cooling, and mechanical agitators for stirring. In the French system the pans are not fixed in a frame, but are separate and suspended on an axis, through which the steam passes; this permits the workman to get somewhat closer to his work, and allows the emptying of the pan by upsetting. Figs. 5 and 6 show an elevation

and plan of a colour pan, with agitators, as constructed by Tulpin Frères of Rouen.

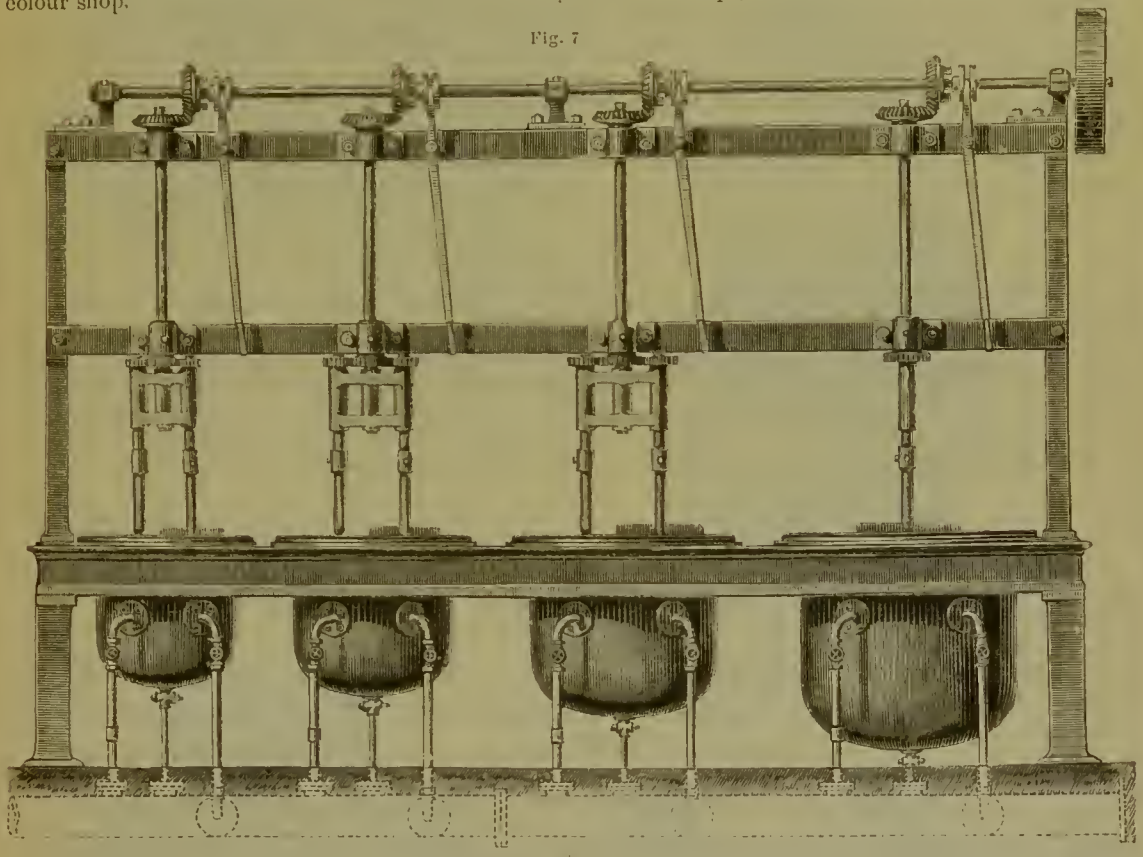
Fig. 7 shows a range by Gadd, and Fig. 9, one by Sumner, both of Manchester. The nature of the agitators are seen in the two sectional elevations of separate pans of Tulpin's and Gadd's construction, Fig. 6 and 8, while still a third variety is seen in Fig. 9.

The French system presents some conveniences, but the pans do not long keep steam tight at the movable parts, and give rise to loss of steam and annoyance. It is found economical to fit steam traps to the waste pipes of the pans, to prevent a waste of steam by blowing through, and to collect condensed water, which is useful for many purposes in the colour shop.

The mechanical agitators, to replace stirring by hand, are of recent introduction; and when well made and carefully managed are both economical and effective. They are not full and complete substitutes for hand stirring, especially with thick paste colours, because they cannot be made to go very close to the pan sides, and a thick pasty mass forms out of their reach which has to be moved from time to time by the stick.

There are very few intelligible instructions which can be given about boiling; the process is simple, and what peculiarities there are in it are special to particular colours. In starch and paste thickenings the material is first made into a homogeneous mass free from lumps, with a small quantity of the liquor

Fig. 7



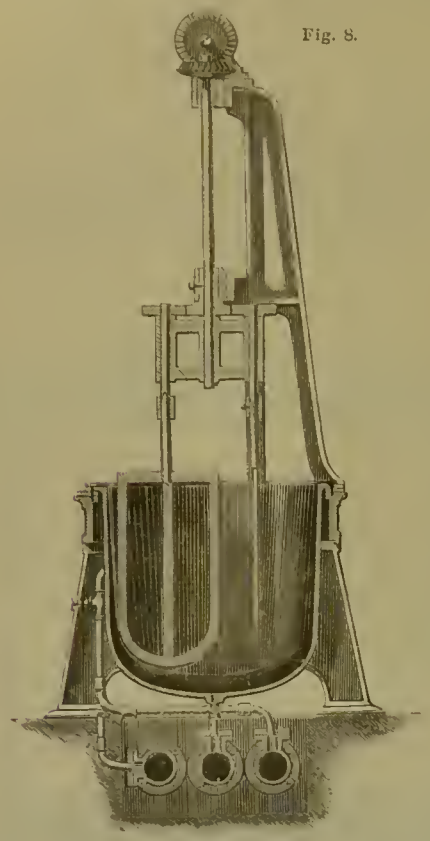
to be thickened, and then the remainder of the liquor added and the boiling proceeded with. Gums do not require this preliminary mixing; if the colour will stand long boiling, as in making gum water, the solution will be effected perfectly; but in mixtures of gum and starch it is well to beat up the mixture with a portion of the liquid before adding the whole. The steam should be turned on with caution, and not too powerfully at first; the boiling should not be continued too long, the only object aimed at being to obtain a smooth consistent mass for printing, and too long boiling injures some thickenings. In all ordinary cases it is a great convenience to be able to cool down the boiled colour quickly, and this is done in the modern ranges by turning on cold water instead of steam, and continuing the movement of the agitating arms until the temperature is reduced to the point desired, either for addition of chemicals or for straining.

Gum water is often prepared by simply boiling up in a suitable vessel, and with a naked steam pipe, the mixture of gum and water, allowing for the water condensed in the vessel.

*Straining of Colours.*—The continental colourists have generally adhered to the system of passing the colours through sieves of wire or haircloth, using the hand or a brush to force thick colours through. The colour is brought by this means into a very suitable state for printing; but it is a very slow and wasteful method, and where the brush is used stray bristles are continually found by the printer under his doctor. The usual hand process in this country is to pour the colour into a square of a strong and open calico, called straining cloth, and then gather-

ing up the corners, by twisting and pressing forcing the colour through. For thick colours this is a very laborious process, and often tests the strength of both the workman and the straining cloth beyond proper bounds. An apparatus for straining by cloth

Fig. 8.



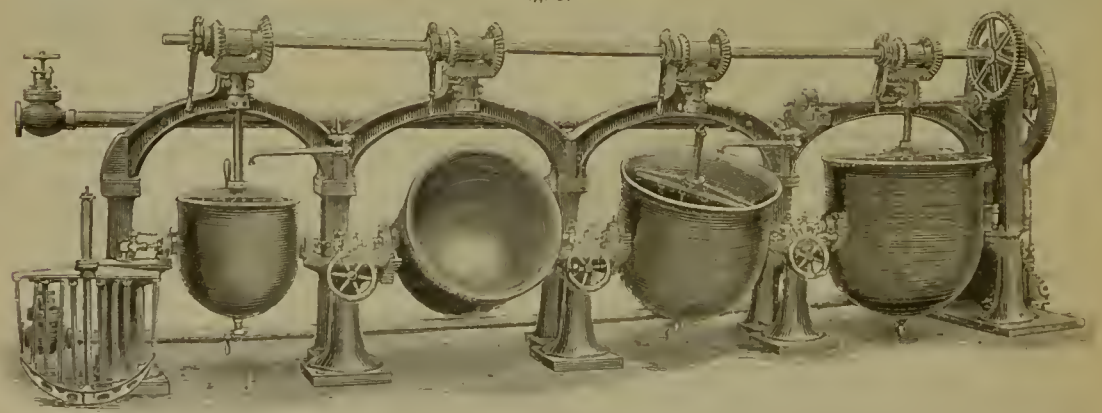
has been recently introduced to imitate the movements of the human strainer. The colour, being inclosed in the cloth, is pressed by being pulled against two small copper rollers, and the twisting is accomplished by an iron arm moving in a frame.

The first fairly successful attempt to apply mechanical power to straining is described in Kay's patent (communicated from Dollfus-Mieg), 9th July, 1856. The apparatus consists of a copper cylinder, supported upon centres in a vertical frame; it is provided at the lower end with a brass or copper grid to support straining cloth or wire-gauze, and above with a closely fitting piston, connected with a rack and pinion, which may be moved either by hand or power to force the piston on the colour in the cylinder, and drive it through the straining material. With a good quality of starch for thickening this straining apparatus works very well; with inferior qualities of starch and flour it is not so satisfactory, forcing many impurities through the sieve, which were better left on the other side. Straining by raising a hollow piston covered with straining cloth in a cylinder filled with colour, as in Rippen's patent, or using hydraulic pressure, as in Ridge's patent, may be considered as modifications of the above.

Figs. 10, 11, 12 illustrate the working of Ridge's straining apparatus, which is favourably reported upon by some firms who have it in use. The colour to be cleaned is placed in B, Fig. 11, and the balanced lid, A, closed and secured. The pump being set to work, the piston, D, which carries the straining surface, C, is forced up into the cylinder, and the colour falls into the receiver, G, and thence into a mug or tub, I. Fig. 12 sufficiently elucidates the nature of the straining surface, C. H is a door on the shoot G.

Many attempts have been made to strain colours by atmospheric pressure, but they have not met with much success, unless the arrangement described by Rosenstiehl, and improved by Glanzmann and Witz in the present year, should be found upon further experience to corroborate the very favourable accounts given of it. The apparatus (Fig. 13) consists of a strong riveted wrought-iron vessel, A, having a capacity of about 130 gallons of water. It is fitted with a pressure and vacuum gauge and four pipes; B

Fig. 9.

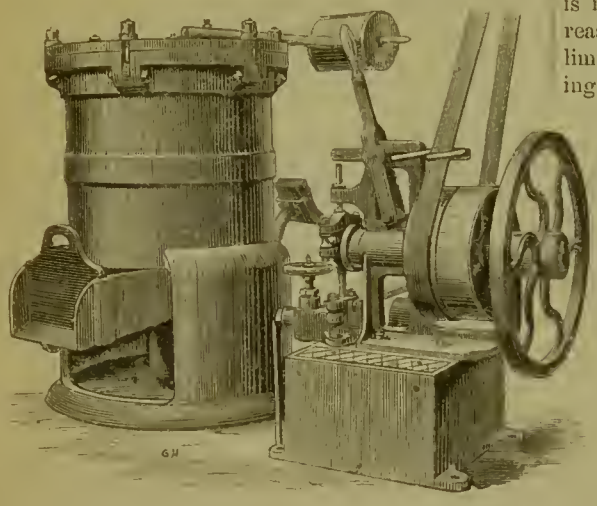


is in connection with a supply of cold water, C is a steam pipe, D is the suction pipe, and E is the discharge or blow-off pipe; the pipe, D, is in connection with a cast-iron vessel; this iron vessel contains the copper or other vessel, *a*, to receive the strained colour; the sieve frame, F, consists of a short wide copper funnel, which contains the wire-gauze or straining cloth, properly supported, and is fitted to go on the iron vessel in an air-tight manner; K shows details of the sieve frame. J, H, and I show respec-

tively a water pipe for cleansing the sieve, the sieve as placed upon a support for washing, and a washing off cistern.

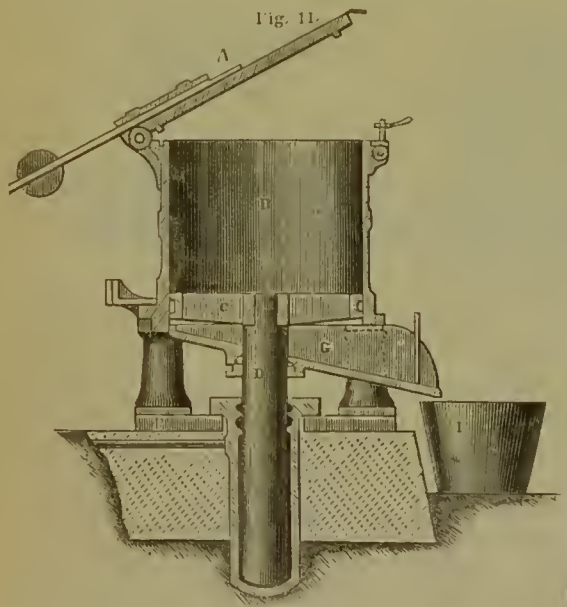
The operations consist in making a vacuum in the wrought-iron vessel, as follows:—The discharge tap, E, is opened, and then the steam tap, C, until steam

Fig. 10.



issues from the end of E; the steam is then shut off and the discharge tap left open a moment to permit the excess of steam to escape, and then closed; water is now admitted by opening the tap of B for a minute, and in twenty or thirty seconds a rarefaction, amounting to as much as 27½ inches mercury, is

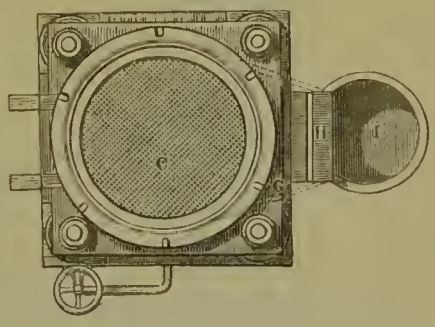
Fig. 11.




obtained. The colour being placed in the strainer, the tap, D, is opened full for thick colours, but only partly for thin colours, so that the colour may not run through the strainer faster than a workman can keep up the supply. One operation gives a vacuum sufficient to strain from 50 to 60 gallons of thin colour, but only from 25 to 30 gallons of thick colour. The process can be rapidly repeated, so that 25 gallons of paste colour can be strained every five or six minutes; in the course of one hour eight or ten different kinds of colour could be strained to the total amount of 200 gallons. The expense of sieving cloth or wire-gauze for three month's work was three francs.*

*Thickening Matters.*—A certain degree of viscosity is necessary in colours for printing, if for no other reason that they may not run or spread beyond the limits assigned to them in the design. The thickening mediums employed in calico printing may be divided into two classes. First in importance are those in most general use, and which are only employed to enable the printer to obtain a good impression from the engraving, and to hold up in suspension the insoluble matters which are constituents of so many colours; those of the second class are more limited in number, and not only give viscosity, but cause the colour to adhere, and to be fixed to the cloth by some change which they undergo in subsequent operations. The thickenings of the first class have only a passing or temporary use; they have to be removed from the cloth in some stage of its treatment, are generally a difficulty and hindrance to the full development of the colour, and the finished print bears no traces of them. Those of the second class constitute an

Fig. 12.




integral part of the colour, just as much as the oil vehicles of an artist; they remain upon the cloth when it is finished, and are the cause of the fixity and stability of the colour. To the first class belong the starches and gums, which are soluble in hot or cold water; to the second belong albumin, lactarine, drying oils, and resinous gums insoluble in water. As the application of the second class involves fewer subsequent treatments of the print than the first, they may be conveniently considered at this point.

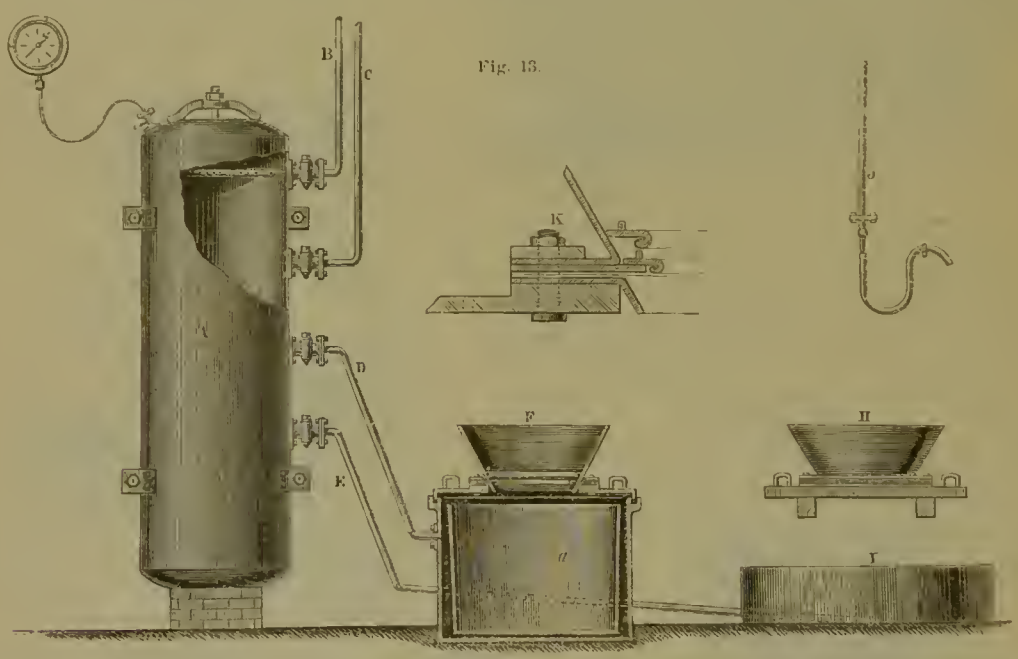
There are only two thickenings of this class of any practical importance, viz., albumin and lactarine. The other thickenings and vehicles which have been tried are gluten, solution of india-rubber, boiled oils, varnishes, and solutions of resins; they have never been largely employed, and do not call for further notice.

* For full details, see Rosenstiehl, in *Bull. de Mulhouse*, 43, p. 430; also *Bull. de Rouen*, April and June, 1875; and *Textile Colourist*, 1, p. 12.

Albumin was at first obtained from whites of eggs. It was used for fixing artificial ultramarine in the year 1845. At the commencement the fluid white of egg was used, afterwards the dried white, as being more convenient and less perishable. In 1854 Pillans patented a process for obtaining albumin from blood. The first products were little suited to replace egg albumin; but experience has at length enabled the manufacturer to supply it in a degree of purity hardly inferior to the best samples of egg albumin, and possessing some properties which render it in many cases preferable. Some calico printers, both at home and abroad, have themselves undertaken the extraction of albumin from blood. This can only be advisable where the local conditions are favourable. As this does not often occur, it is sufficient to refer to the description of the process in the *Bulletin of the Industrial Society of Mulhouse*, vol. 39, p. 214.

The solution of albumin is prepared by stirring the powder in cold, or, what is better, in slightly warm water; hot water, of course, coagulates it. Blood albumin thickens better than egg albumin, requiring a less quantity per gallon of water. From 1 to 5 lbs. per gallon of egg albumin should give a sufficiently thick solution. To a certain extent the addition of Senegal, or other gum water, does not conspicuously injure the fixing power of albumin for either pigments or dyes. With one-fourth of gum water, or even one-third, those colours which only require cold washing or slight soaping are good. Mixing with an equal volume of gum water does not destroy the fixing powers of albumin; but the colours will not wear well, and are only fit for low class work. For the application of pigment colours along with alizarin, or any other colour that requires soaping to finish it, the use of egg albumin without gum water is recommended. Blood albumin

Fig. 13.




in these styles may be employed, but it is not so good as egg, neither holding the colours so firmly nor showing them so brightly at the end, probably because this kind of albumin seems to take colour from tinged soap liquors more freely than egg albumin.

Albumin solutions are liable to enter into putrefaction and smell very offensively, and there is no perfectly effective means of preventing or arresting this decomposition; but the putrefaction must be very far advanced before the albumin is unfit for use. Solutions which are opaque from insoluble matters become much clearer by slight decomposition, which changes the cellular tissue into a soluble but non-coagulable substance, leaving the albumin practically uninjured.

The working of albumin colours in the machine is sometimes attended with considerable difficulty from excessive frothing, and from the pigments sticking in the engraving. The fault lies either in the albumin being inferior or containing much insoluble matter, or from the solution being unskilfully prepared, or from the pigments being incompletely incorporated with the solution. The two last faults can be corrected by attention and care; the first admits only of alleviation, by dissolving the albumin as hot as can be done without coagulating, settling and straining well, and adding a considerable dose of ammonia, turpentine, or naphtha, as circumstances seem to require and the nature of the colour permits. The pigment green (*Vert Guignet*) is a colour which has given much trouble by sticking in the engraving, and it has been thought necessary to use a brush furnisher, set with tolerable pressure against the roller. This contrivance prevents the accumulation of the pigment in the engraving, and renders it possible to continue printing; but it does no more than keep constantly cleaning out a deposit which

ought never to form, and which, if it forms to a notable extent, makes the impression very inferior in fulness and smoothness. In this and every similar case the colour-mixer is bound to try and supply the printer with a colour which will work without a furnisher, or with an ordinary plain furnisher. To continue the case of the pigment green, it has been found possible to print say 50 pieces at once without changing the colour and without brush furnisher, the impression being all that could be desired; and with the same materials put together by another hand, it is impossible to print 3 yards without brush furnisher, and helped by the printer brushing the roller by hand, and after all giving a very inferior impression. This is evidently a fault in manipulation: other faults in the materials may occur. It happened the writer had to use a cheaper kind of the pigment green; and with good albumin solution the printer could not print three turns of the roller without the engraving being filled. The new pigment was examined, and found to effervesce with acids. Dilute nitric acid was carefully added to a quantity of the albumin colour, and the colour sent to be tried again. This haphazard remedy was perfectly successful, and afterwards acetic acid was used in all cases when a similar difficulty occurred. But no skill suffices to get good results from some materials, and there is nothing left for the colour-mixer but to show clearly which of the materials employed is defective.

Albumin may be bad from imperfection in its manufacture or from adulteration. There are no accurate methods of testing small samples chemically, the only trustworthy test being by comparison with a known good quality.

Lactarine, or caseine, is the dried curd of milk. It was introduced by Pattison in 1848. Unlike albumin, it is insoluble in water, but swells out into a state of quasi solution under the influence of ammonia. It forms a smooth white paste, which, when in good condition, prints very well. Pigments and dyes applied to lactarine are sufficiently fast for many purposes, but are inferior to those fixed by albumin. The lactarine solution is liable to spontaneous coagulation from unknown causes. It sometimes goes curdy in the colour box while working, and seldom keeps good for twenty-four hours together, so that a colour which has been once used in the machine can seldom be employed a second time. This uncertainty has much restricted its use; but with care and intelligence it can be profitably employed in the lower classes of prints, or for those styles which do not need much washing off. A high temperature is injurious to lactarine solution, and it should be kept in the coolest place available.

The fixing of colours made with albumin and lactarine is by steaming, and is due to these thickenings becoming insoluble in water by the heat, and so cementing the colours to the fibre that they adhere with great tenacity. Applied in large masses to the cloth, they give it an objectionable harshness and stiffness, which can be partially removed by washing. These colours are sometimes fixed by running the cloth into boiling water, and it is thought that finer shades, especially of ultramarine blue, are thus obtained.

The other thickening matters in use in the colour shop consist of flour, various kinds of starches, and mixtures of flours and starches, natural and artificial gums.

The paste thickenings are those in which the thickening matter swells up upon being heated with water, and are principally represented by wheaten starch and wheaten flour.

Wheaten starch of good quality is one of the most reliable thickenings in use. It thickens sufficiently well at about 1¼ lb. per gallon of water, and next to tragacanth offers the least resistance to the reaction of the constituents of complex colours, and the least obstruction to the passage of mordants from it on to the cloth. It is essentially a watery thickening, containing only from 10 to 12 per cent. of solid matter, has a large capacity for dissolving salts, and penetrates the cloth to a considerable depth, even passing through the usual thicknesses of printing cloth. Unless combined with a considerable portion of soluble salts, as in some steam colours, or unless mixed with some of the soluble thickenings, it is difficult to wash off from the cloth after hard drying; it is therefore chiefly used for those styles which can bear a fair amount of washing as good steam colours, or for dyed styles which can be submitted to a hot water treatment.

The quality of a sample of starch, or its fitness for use as a thickener, can only be ascertained by trial; but the characters of a good starch may be defined as consisting in a taste free from acidity, colour not necessarily bright white, but uniform and free from specks, a fracture not too flinty if in so-called crystals, and a freedom from sand or mineral matter. Carelessly made starch contains insoluble substances which interfere with printing; these are bran, husks, and straw. They can be detected by mixing the starch with cold water, and observing the floating matter, and what settles at the very bottom, and what on the top of the starch. Starch which contains glutinous matters is very unreliable; it is very fermentiscible, and does not give a tenacious thickening. Very white starch is sometimes found weak, probably injured by chemicals used to bleach it. If such a starch requires 1¾ to 2¼ lbs. to thicken a gallon of water, the colour mixer may expect a great disturbance in all his colours arising from that fact. If there are complaints of bad working of starch colours in the machine, an intelligent examination of the starch will generally indicate the cause, and the best remedy is to change the supply. The printer of this day, working fine colours like alizarin red, pink, and purple as topical colours, should spare no trouble or expense to secure a first-rate quality of starch, for it simplifies very much the whole process of printing.

Other starches than wheaten starch have been proposed for use, but none are so suitable; the various paste thickenings in the trade are indefinite mixtures of different feculous matters, the suitability

of which for particular purposes can only be known by practice and experience.

Wheaten flour as a thickener is nearly restricted to dyed styles and to mordants of a simple nature, such as red liquor and iron liquor, or mixtures of these two. For this purpose it is extensively employed, as being an economical and perfectly safe thickener. The flour should be of a good quality, finely sieved, free from grit, and while not too rich in gluten, should be capable of yielding a tenacious sound gluten when kneaded in a current of water. Flours which contain a high percentage of gluten never work well; the paste is too tough, and in working some gluten is liable to separate and get into the engraving. Flour in which the gluten has been injured by the weather or bad storage, gives a poor, short, watery paste, incapable of fine printing. The complex constitution of flour makes it unfit for thickening colours containing active chemical agents; and its tenacious adherence to the fabric, and resistance to gentle washing, confine its use to those styles which have to be dunged, dyed, or soaped.

Tragacanth, though called a gum, is properly reckoned among the paste thickenings. It is the most powerful thickening material we have, 1 lb. of it giving sufficient thickness for printing to 4 gallons of water. When of good quality, it yields a very smooth and evenly pasty mass, which when price permits may be advantageously employed in many styles of printing. Containing so much water, it is of course deficient in what is called solidity, does not answer for outlines, penetrates the cloth very freely, and offers so little obstruction to the communication of the mordant or colour to the cloth, that with it the very darkest shades can be obtained of all colours. It washes off well, and on account of the very slight stiffness and harshness which it leaves upon the cloth, it is very suitable for those styles which are either not to be washed off, or which permit of but a very slight washing.

Tragacanth is much employed by continental colourists in small proportion along with starch and gum thickenings. It is believed by them to communicate very valuable properties to other thickenings, and is found in a vast number of recipes where it is never used in English colour mixing.

Natural gums have been used from time immemorial as thickeners for calico printing, and are still extensively used when scarcity and a high market price does not drive the printer to substitutes in the shape of artificial gums. The type of the natural gum is gum arabic, which is entirely soluble in water, and gives a smooth oily fluid, running uniformly and without pastiness; the cheaper gums used in the trade are called gum Senegal, gum Gedda, Turkey gum, East India gum, &c. They are all exudations from similar shrubs and trees, and should only differ from one another by the respective amounts of impurity acquired in a more or less difficult or careless gathering of the gums. In so far the value of these gums might be estimated in the inverse ratio of the insoluble matter, such as sand, gravel, sticks, and leaves, contained in them. But there are trees which yield gummy exudations of quite another character, and so nearly resembling in external characteristics the soluble gums, as not to be easily distinguished from them, and they are used to mix and adulterate the proper gums. A good gum dissolves completely in cold water, but the inferior gums only swell out and give clots and semi-pasty masses, stringy and glutinous. By themselves these pseudo-gums could not be used, but when boiled up with a proportion of genuine gum they become diffused through the mass; and such mixtures may be employed for certain colours and styles where great clearness of colour or smoothness of impression is not required.

Natural gums, unless hand-picked, always contain so much sand that they cannot be safely used for machine printing except first made into gum water; as the gum water while hot is thin, the sand easily settles out. The gum water is made by simply boiling the gum and water together, about 6 lbs. per gallon for thin, and as high as 12 lbs. per gallon for thick gum water. The acidity which developes in gum water in warm weather appears to be owing to the formation of acetic acid, and is not usually detrimental to any of the colours or mordants for which gum water is employed.

The natural gums are usually employed for the lighter shades in steam colours, and for catechu brown in dyeing; for block-printing they can be used for all colours, except the darkest; being soluble they wash off easily, and leave the cloth soft and fine to the touch.

Artificial gums or gum substitutes were introduced in the early part of this century, and have proved at various times a great relief when circumstances have caused an interruption in the supply of the natural gums. They are made by roasting, or calcining, as it is called, the various kinds of starches or farinas, as wheaten starch, rice starch, potato starch, sage flour, &c. By some change which takes place the globules, which were quite insoluble in water, are rendered almost completely soluble; they no longer produce pastes upon boiling, but gummy solutions, but does this at a great expense of material. Wheaten starch, which gives a good paste at $1\frac{1}{4}$ lbs. per gallon, yields a gum water which requires five times that amount per gallon of water, and of other starches even a greater relative proportion is required to produce a suitable thickness.

The chief artificial gums in use are calcined farina, British gum, and light-coloured soluble gums

Calcined farina is made from potato starch; it is a weak gum, requiring from 8 to 10 lbs. per gallon of water; when properly made it is the most gummy of all the substitutes, and remains fluid for several weeks; from its density and smoothness it is an excellent printing medium, reproducing accurately the finest lines and stipplings of the engraving, and for dyed work giving soft and agreeable shades. The weight of solids in the thickening renders it impossible to obtain dark colours from it, and it is hardly ever employed except for iron mordants intended to yield light shades of purple in madder

and alizarin dyeing. Its dark colour is objectionable for topical application; it might be made much lighter than it is usually sold with advantage; being very soluble, it easily washes off.

British gum is made from wheaten starch, roasted either light or dark, giving rise to what in the first case is called light British, and the second to dark British gum. The light gum thickens at from 2½ lbs. to 4 lbs. per gallon; it is half pasty and half gummy, and very suitable for mixing with paste thickenings and for a large class of steam colours. Unless when used with metallic salts in excess, it easily washes off; but in this property regard must be paid to the amount of unaltered starch which it contains, and which is very variable.

Dark British gum thickens at from 5 lbs. to 6 lbs. per gallon of water, and finds its principal employment in dyed styles; it is an excellent thickener for heavier shades of purple from iron liquor mordants; as a thick gum water it is useful to add in certain proportion to flour or starch thickenings; it is the proper thickener for the alkaline aluminate mordant, and generally suits well for all shades which have to be raised cold, as iron buffs and other metallic colours. Compared with calcined farina it is somewhat puffy, and does not yield as fine an impression; and when made from inferior qualities of starch is liable to contain black particles difficult to strain out, which stick in the engraving and spoil the printing; it is also particularly liable to frothing while working.

The light soluble gums are made from different starches by the aid of weak acids or acid salts, and with a much slighter roasting than is employed in the case of the gums just described. When of good quality they are quite soluble in cold water, and the solution is not more coloured than a solution of natural gum of the same strength. They are employed in cases where a coloured gum is objectionable, as in printing woollens, delaines, and paper, and also where a thickening is desired which will easily wash off. These gums are very variable in thickening power, and generally of an unreliable nature with colours which contain metallic salts, excepting alumina, which does not seem much influenced by the saccharine and acid principles contained in most qualities of soluble gums. They should never be used for mordants; and generally every fresh supply should be practically tested before using, on account of the variation in the degree of acidity and other objectionable features of this article.

Of the various other thickenings sold in trade nothing need be said; whatever names they may bear, they will be found to consist of one of the gums described, or mixtures of them with flour or some kind of starch.

The fitness of a colour-mixer depends so much upon his ability in managing the thickenings he has to employ, that he cannot give too much attention to this point, nor study too minutely their properties and behaviour with mordants and the cloth to be printed. The first thing in a colour is that it shall work well, give a good mark, and not trouble the printer. If it does not fulfil these conditions there is something wrong in the thickening. It may be that the thickening itself is of a bad quality, or that unsuitable thickenings have been used, or they have been put unskilfully together. It is manifestly impossible to go into complete detail upon this point. There are hundreds of colours used in printing, and each one has its own peculiar properties; some generalities, however, may be touched upon with advantage.

Frothing in gum colours may be traced to the thickening; it is usually kept down by means of oil, naphtha, turpentine, petroleum, tallow, &c. The non-volatile oils must be used with caution in mordants for dyeing, as they influence the shades, especially purples in madder dyeing.

Scratching of the roller is due to grit or sand, or other hard particles, as crystals of potash salts, burned starch, &c. There is hardly any remedy for fine grit in the gum or starch; it cannot be strained out; there is nothing to be done but to choose thickenings as free as possible from it. To ascertain beforehand the amount of grit, sand, and generally insoluble bodies likely to prove troublesome in a gum, boil it with water containing sufficient muriatic acid to take all the thickness out of the gum, and examine the sediment which deposits after a sufficient interval. Crystals will be found to be generally sulphate, bitartrate, or chlorate of potash. The remedy is to use the colour a little warm, or not to let it cool down to the crystallizing point before using.

The corrosion of the doctor edge, and consequent injury of the roller, is a very troublesome defect, and its cause generally difficult to trace. Probably chlorine in a nascent state exists in such colours as aniline black, catechu brown, or steam colours where metallic nitrates, chlorides, chlorates, and free acids are present; and these are the colours which act upon the doctor. Cases where the doctor edge is roughened by such simple colours as madder red or black not unfrequently occur; they are impossible to explain, and are generally cured by making fresh colour, or even changing the colour to another machine, where probably some slightly different arrangement of the parts prevents or gives rise to a different electrical condition of the roller; for to such condition of the roller or doctor it is usual to ascribe these otherwise inexplicable accidents. Where very active chemical salts are present, such as copper salts and chlorates, the point to attend to is to use the least possible quantity of the salts, to put them into the least active condition, and have as dense a thickening as the colour will permit.

Sticking in the engraving, previously referred to when treating of pigment colours, only takes place when insoluble matters are in the colour, and when the thickening is not of a suitably adherent nature. The colour taken up by the engraving is, so to speak, filtered by the cloth at the moment of the printing, and the soluble and insoluble parts separated; the soluble penetrates the cloth, some of the insoluble rests on the face of the cloth, and some remains in

the engraving, and the result is more or less inferior. This defect is common to all pigment colours, to catechu brown and many steam colours. Something can be done to remedy this by the printer using less lapping, and printing with the least possible weight; but the colour mixer should endeavour to obtain the most perfect division of the insoluble matter possible, so that every particle or molecule may be surrounded with a sphere of the thickening, which must be dense enough to hold it in suspension.

A colour working thick in the machine is owing to bad thickening or bad boiling. There is a thin gum and a thick gum or paste badly combined and not completely dissolved, and they separate under the doctor, the thin gradually leaving the colour, which becomes thicker and unworkable.

The depth of shade given by a fixed proportion of mordant or colour bears a close relation to the weight of thickening employed; the smaller the weight of thickening the darker the colour; hence tragacanth and starch give deeper colour than gums. The depth to which a colour penetrates is governed in a great measure by the same conditions; the more watery the thickening the greater the penetration, a point worthy of consideration for dyed styles, where the amount of dyestuff to be used is regulated by the degree of penetration of the mordant. The colour mixer and the printer should aim at keeping colours as much on the surface as possible; only very deep colours are improved by penetrating the cloth, all others are injured.

STEAMING PROCESSES AND STEAM COLOURS.—Drying after printing by machine is usually accomplished by means of steam chests, of which there are a sufficient number (from fifty to sixty) to insure the thorough drying of the heaviest patterns. The English steam chests are of cast iron, small, and very heavy; the continental steam chests are of wrought iron, riveted, with not more than 1 inch of steam space, and are made 6 or 8 feet long, and may be curved. The point to be attended to is that the pieces are quite dry, yet not heated to an unnecessary extent; that is, the number of chests, the amount of steam on, or the speed of printing, must be so arranged that the piece has not to pass over or close to more than two or three chests after it is dried, and this because many colours and mordants are greatly injured by over drying. On the other hand, under drying must be carefully avoided as the greater evil of the two.

After drying the course taken by the printed piece depends upon what has been printed upon it; and as we gave precedence amongst thickenings to the vehicles for pigment colours, it will be convenient to proceed as if the pieces had been printed with pigment colours, or other colours requiring steaming without the necessity of ageing, and the subsequent processes which belong to dyed styles.

It is believed that the process of steaming for fixing and developing colours is an English invention, practically applied at the beginning of this century. It was probably independently discovered in France about the same time, for after the close of the wars, and the renewal of peaceful intercourse in 1815, we have it recorded that two Frenchmen came to sell the discovery of steaming to the British printers, but were met everywhere with the statement that the thing was old and well known. The one chief way of steaming pieces now practised is to have a steaming box, house, cottage, or kennel, generally constructed of iron and preferably of boiler plate riveted, and of a circular or oval form, provided with a door which can be securely and tightly closed, and pipes to admit and let off steam. The goods to be steamed are hung by various contrivances upon a frame which can be rolled into the steaming house, and are there subjected to the action of the steam.

Besides these modes of working, arrangements have been devised for continuous steaming, but they are too recent in their application to enable anyone to say whether they will turn out of practical advantage to the trade. Reference may be made to the patents of CORDILLOT & MATHER, Feb. 9, 1875; SMITH, April 10, 1875; JONES, August 21, 1865; and also THIERRY-MIEGS process, April 29, 1875. (See *Textile Colourist*, vol. i. pp. 97, 98, 106, 400.)

Fig. 14 shows a sectional elevation of steaming cottage with the goods hung on the frame, which travels on a railway. Fig. 15 is an end view of the same with the door closed. The wheel on the left of the door is connected with a light shaft running the length of the frame, and geared to each of the suspending rollers. By turning the wheel the position of the cloth is changed, and irregularities from contact with the rollers in great measure avoided.

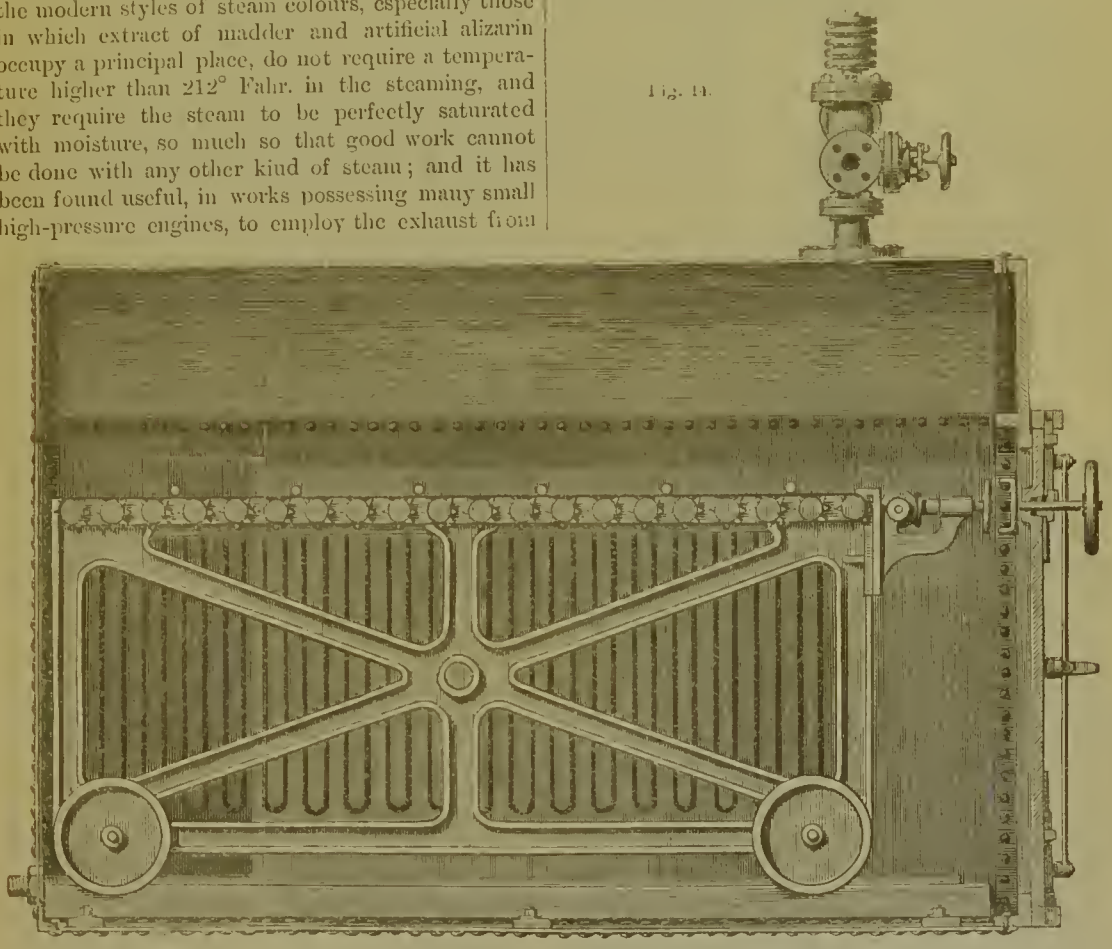
Pigment colours fixed by albumin are the simplest of all colours to steam; they require nothing but thoroughly heating through, and they are not easily injured by carelessness or unskilfulness. Yet this facility has led frequently to under steaming, which is shown when the goods are washed off, by the loss of colour all the length of the piece in its centre, while it is perfectly fixed at the edges. For other colours on calico the steaming operations may present more or less difficulty, according to the number of colours on the print and the delicacy of the shades to be obtained. Only a few cases can be cited and general rules given. The great bulk of colours on calico require nothing but a sufficient quantity of low pressure and moderately damp steam. Most of the inferior results traceable to steaming are owing to having the steam too dry and too hot, and this is sometimes difficult to avoid if the steam be supplied at a pressure superior to say 10 lbs. on the square inch. There may be water at the bottom of the steaming box, and the steamer supposes that therefore the steam must be wet; but notwithstanding this the steam may be so dry that the goods never get really softened, and the colours are not in a position to develop themselves or combine with the cloth. It is desirable that the steaming boxes should be supplied from low pressure boilers, working at from 6 lbs. to 8 lbs.; or if there is only a high pressure supply it is useful to have a receiver of strong

boiler-plate, having a capacity of several cubic feet, placed between the boiler and steaming box, provided with valves and gauges, so that the steam may be reduced under the eye of the steamer himself. This arrangement is in use on the Continent, and it is a palliative, but nothing more; for dry steam does not become damp with that rapidity which would at first sight seem likely, and cannot instantly saturate itself, even in contact with water. Many of the modern styles of steam colours, especially those in which extract of madder and artificial alizarin occupy a principal place, do not require a temperature higher than 212° Fahr. in the steaming, and they require the steam to be perfectly saturated with moisture, so much so that good work cannot be done with any other kind of steam; and it has been found useful, in works possessing many small high-pressure engines, to employ the exhaust from these engines for steaming madder extract and alizarin goods, and thus insure a really moist steam.

In some cases of mixed and woollen goods, with dark colours, a high pressure of steam is thought desirable for at least a portion of the time during which the goods are under treatment.

In order to prevent the liberated acids or other vapours from injuriously affecting fine colours, a

Fig. 11.



large volume of steam should be allowed to blow through during the first part of the steaming. In steaming alizarin styles well covered with colour, a very large quantity of acetic acid is set free, which may influence other colours, and even rapidly corrode the iron plates of the steaming box. Vessels full of slaked lime have been placed at the bottom of the box to absorb this acid, and greys padded in a chalk mixture wound on with the pieces, but it is preferable to have a free current of steam blowing off.

The time to be allowed for steaming varies from half an hour to three hours, depending upon the styles, the quantity of cloth, and the pressure or volume of steam; those colours, such as dark chocolates, cochineal scarlets, blacks, and extract and alizarin colours, which do not contain a large proportion of soluble salts, and which dye, so to speak, the fibre, demand the longest time in steaming; but the composition of these colours can be largely varied, and no general rule can be given.

To avoid unevenness much care is required in some styles, and steaming boxes are usually provided with apparatus by which the cloth can be moved without interrupting the steaming, so that, as far as possible, every part may receive a due allowance of steam; and in some cases the pieces are hooked on a frame or suspended by cords, in order that the steam may pass freely through every fold.

To prevent marking off a grey piece is frequently wound on with the printed piece. It is desirable to ascertain the absence of matters in the grey which might injure the colour.

Colours containing copper and lead are liable to become darkened by impure steam containing sulphuretted hydrogen. This fault is in the boiler, and no good can be done until the boiler is cleaned; some relief, however, is obtained by hanging up

calico saturated with acetate of lead. A certain metallic lustre, apparently not due to sulphur, is frequently developed in some dark steam colours; this arises from the colour itself, and is generally remedied by addition of sal-ammoniac to the colour. The darkening and sometimes almost decolorizing of pigment orange made from minium, is owing to acid in the steam, which decomposes the colour, forming the puce-coloured oxide of lead. This does not occur with orange made from the chromate of lead.

Accidents from drops of condensed water, or running caused by undue condensation of steam upon the cloth, are to be guarded against by prae-

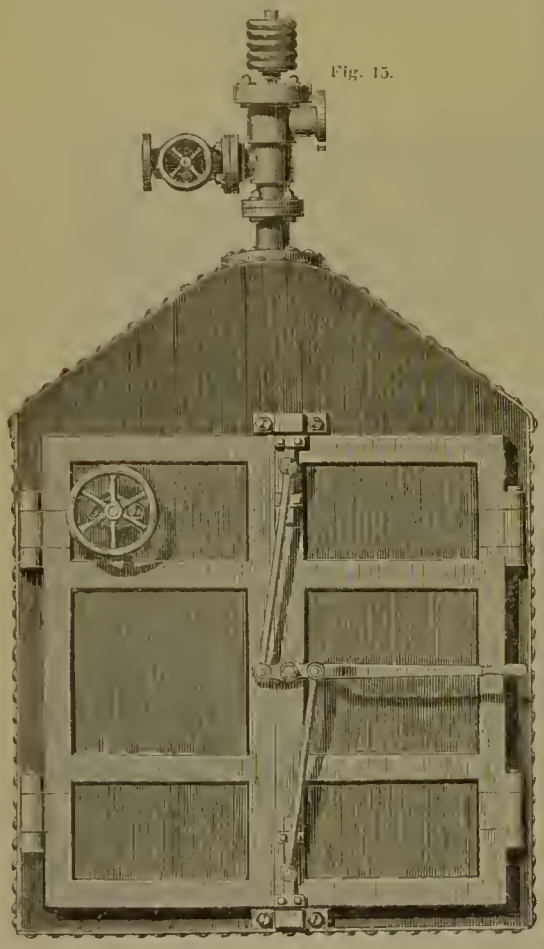


Fig. 15.

tical precautionary measures, such as warming the box before commencing, seeing that the cloth is not too cold in entering, and covering exposed parts with thick woollen blanket.

The majority of steam colours are simply washed in water after steaming, and require only finishing, others require special treatments, which are more properly considered further on.

Mordants for Dyed Styles.—We now proceed with the dyed styles, the colours or mordants on which require some kind of ageing, fixing, and dyeing, and as the successful working of these styles depends greatly upon a knowledge of mordants, it is desirable at this point to consider them.

The various fibres used in manufacturing textile fabrics differ considerably in their behaviour to chemical agents, and it is impossible to treat them generally as having the same character. The following remarks are to be considered as applied to cotton goods when other fibrous matters are not expressly named.

Of all the organic colouring matters which exist in nature, and all those which modern chemistry has manufactured by art, there are hardly half a dozen which give a tolerably full shade to cotton without the assistance of some intermediary agent; and with the exception of indigo blue and aniline black, both of which are applied to cotton in an unformed state, they are all of the most fugitive and unstable character. The most powerful and most valuable colouring matters, as madder, alizarin, logwood, brazil wood, cochineal, quercitron, bark, and fustic, however applied to cotton, communicate to it only a dull stain, which can be nearly all washed out with water, and which is incapable of resisting the action of air and light. At a very early period it was discovered that certain mineral salts, and some vegetable and animal substances, were capable of contracting a very intimate alliance with cotton; and though these substances themselves possessed little or no colour, they enabled the cotton to retain the colour from dyestuffs in a very perfect manner. In modern times the number of these intermediary substances has been increased by some additions, and they constitute the class of mordants, which name is properly applied to any matter which has the power of combining at the same time with the cloth and the colouring matter.

The mordants may be divided into three classes —first, those derived from the animal kingdom; secondly, those from the vegetable kingdom; and thirdly, those from the mineral kingdom.

The animal mordants are albumin, lactarine or caseine, and gluten. It will be observed that these are all highly nitrogenous bodies, and of complex composition; they are soluble in water or alkalies, and by heating become insoluble, and thus can be securely fixed on the cloth. Their use as mordants is but limited, and at the present time does not extend beyond the application of aniline colours. The treatment is very simple; a solution, say of albumin, is made, and the colouring matter added in proper proportions; the mixture printed and steamed, when, if required, the goods may be washed or slightly soaped. If the albumin alone were printed and steamed, and then the goods dyed in a solution of the colouring matter, the albumin would be found to act as a mordant; but it is not advantageously used in this way. The solution of lactarine has been largely used to mordant or prepare calico and mixed goods for printing steam colours upon, and very pleasing effects were produced; but the expense was considerable, and the processes now little used; lactarine is a suitable mordant and thickening for the topical application of the coal-tar colours, which are not injured by alkalies. Instead of the commercial lactarine, inferior

qualities of cheese made from skim milk, and deprived of fat, may be dissolved in soda or ammonia. Gluten has been applied, but does not seem well adapted for the purpose.

Glue or gelatine might be included in the animal mordants, but its properties differ considerably from the others; it does not become fixed or insoluble without the aid of some vegetable or mineral substance.

The vegetable mordants are of a dubious nature, and hardly any of them can be said to satisfactorily fulfil the real conditions of a mordant, and it is probable that further research may remove them out of the class altogether; they are confined to the various astringent substances, whose type is tannic acid, and to fatty matters, represented by olive oil. Both astringents and oils can combine in an intimate manner with cotton, and they have a certain but very restricted affinity for colouring matters, and only act as perfect mordants for the majority of colouring matters when they are used in conjunction with mineral mordants. However, tannin or tannic acid is employed to fix several of the aniline or coal-tar colours by simply thickening, printing, and steaming; the result is not very good, whether regarded as a fast colour or a brilliant one. By passing the steamed goods through metallic salts, such as tartarized antimony, as in LLOYD and DALE'S process, some farther degree of stability is attained; but on the whole, this use of tannin matter is very limited in printing, though very extensively employed in piece dyeing, either with or without other mordants.

The use of oily compounds to fix the aniline colours seemed at one time to promise useful results. The oleate of ammonia was employed with some success, but it has not satisfied practical requirements. The mixture of oil with the majority of colours for printing has nothing to do with its power as a mordant, although, as before stated, its mordanting powers sometimes interfere in a hurtful manner.

The use which is made of oil in turkey red dyeing is only remotely connected with this subject; it is but little understood, or cannot be used in a similar way in calico printing. It has often been proposed to prepare calico for printing various colours by a modification of the oiling process used in turkey red dyeing; but it is not proved that any advantages have resulted from the attempts thus made to give increased stability or brilliancy to topically applied colours.

The mineral mordants are those most employed for general dyeing purposes, as also for calico printing, and consist of salts of the metals, and chiefly those of alumina, iron, tin, and chromium.

Alum and salts of alumina have been in use from ancient times, though it cannot be clearly shown that the acetate of alumina, as at present employed, was known more than about a hundred years back; the oldest recipes contain several ingredients of apparently a useless nature, such as arsenic; but it is only stated in a few cases that the arsenic was to be dissolved in potash, which quite changes the nature of the addition, and with the use of vegetable acid solutions at the same time produced a species of mordant approaching to the modern red liquor. In 1742 there was a patent granted to DANIEL CHAPPEL for a mordant composed of alum, arsenic, white argol, chalk, and saccharum saturni (acetate of lead), all mixed together in liquor thickened with gum arabic. If the proper proportions were used, and as little as possible of the arsenic and argols, a perfect red mordant for light reds at least could be made by the patented process, which contains the first distinct mention known of the use of acetates to decompose alum.

Alumina may be considered as the perfect type of a mordant. It is itself colourless, and has therefore no physical or complementary optical influence upon the shade produced by its combination, and is capable of being saturated to a high degree with most colouring principles, and giving distinctive and definite hues with nearly all dye woods.

The acetate of alumina of the printers is prepared from alum, or sulphate of alumina, and acetate of lead or lime; the proportions to be used may vary within narrow limits, and for special styles particular additions are made generally without any necessity. It is sufficient to give here two practical recipes for each of the ingredients for red mordants which have been in use for several years, and which properly thickened and reduced have satisfied every requirement for reds, pinks, and chocolates. A strong red liquor is made by taking 100 gallons of boiling water, 480 lbs. of alum, and 384 lbs. of white sugar of lead; this should stand at about 20° Twaddle, and is the strongest red liquor that need be made. Another standing at about 12° Twaddle is composed of 150 gallons of water, 460 lbs. of alum, and an equal weight of acetate of lead. It will be observed that these red liquors, besides their difference in strength, must have an essentially different internal composition, and, it may be concluded, a very different behaviour in the various conditions in which they are placed in practice. This is undoubtedly so, but not to so great an extent as might be imagined. The second red liquor was found to be very well suited for full reds, as well as for chocolates; but it is on the whole what may be called an unstable mordant, and could not be depended upon when reduced with four or five volumes of water for light reds and pinks, even with a free addition of acetic acid. The first red liquor was found of very general applicability in dyed styles, and was used with confidence for all colours, and preferred for everything except for a full bright red, for which particular colour it never gave so good a result as the other. It is not unusual in making red liquors from acetate of lead to add about 10 per cent. of the weight of the alum of crystals of carbonate of soda, after the principal ingredients have been well mixed, or an equivalent amount of ground chalk; on the large scale this addition may be found economical, but for colour shop practice it is generally considered safer to use a little more acetate of lead, if necessary, than trust to the effect of either soda crystals or

chalk. Acetate of lime is largely used as a substitute for acetate of lead, and would answer nearly as well if its quality could be depended upon with as much confidence as can be reposed on the acetate of lead; but acetate of lime, either dry or in solution, is liable to variations in composition, which have produced very disagreeable irregularities in practice. Sulphate of alumina is also used instead of alum, but like acetate of lime it does not present any external appearances by which its purity or strength can be determined; it is not constant in composition, and cannot consequently be depended upon with the same certainty as the well-defined crystals of alum. For these reasons the majority of colour-mixers, who make their own red mordants, adhere to alum and white acetate of lead; but with sufficient chemical knowledge to ascertain the real value of the materials, perfectly satisfactory results can be obtained from acetate of lime and sulphate of aluminia, and there is some economy in employing them. Two red liquors which have been in use for many years, in which acetate of lime and sulphate of alumina are employed, were made as follows: — 50 gallons of acetate of lime liquor marking 24° Twaddle, placed in a copper pan, and heated up to 140° Fahr., and 200 pounds of ammonia alum in a crushed or roughly powdered state added. The temperature is maintained at 140° Fahr., and the mixture kept constantly stirred until the alum is perfectly dissolved, which may take two or three hours, then 12 lbs. of ground chalk are added in small portions with stirring. The resulting red liquor should mark about 20° Twaddle, and should be good for all dyed reds and pinks. It will be more or less darkly coloured according to the colour of the acetate of lime; the sulphate of lime bottoms are very bulky compared with sulphate of lead bottoms, and retain a great quantity of mordant, which can be separated either by pressing or washing. Another red liquor was made from 90 gallons of the same acetate of lime liquor, and 272 lbs. of sulphate of alumina, with addition of 34 lbs. of ground chalk, using the same general procedure. The resulting red liquor marks about 16° Tw.; it is capable of yielding good reds and chocolates, and was found to work well with considerable addition of tin crystals in the case of reds required to resist covers of purple or chocolate.

The only other alumina mordant in use for dyed styles is the aluminate of potash. Its use was suggested at a comparatively remote date, but it has never come into general employment. The usual method of preparing it is by adding powdered potash alum, or sulphate of alumina, to boiling caustic potash; for each gallon of the latter marking about 51° Tw., 3 to 3½ lbs. of sulphate of alumina may be employed. The heating and stirring is maintained until the salt has quite disappeared; upon cooling sulphate of potash crystallizes out, and the clear liquor is the mordant. It cannot be properly thickened by starch, flour, or the natural gums; it is best thickened with well calcined wheaten starch. In some works it is considered that aluminate of potash is the most preferable mordant for pinks; but the opinion is by no means general, and as the fixing requires special means not in use for the general run of dyed goods, it is not largely employed. It is difficult to say what advantage it has over the acetate of alumina mordant for madder or alizarin pinks, except in the printing. It gives a very clear impression, but what is most important, it is not injured by too much heating in the steam chests. The weak acetate of alumina mordants intended for pinks, whether thickened with paste or gum, require very great care in drying after printing—if too much heated the mordant is greatly injured; with aluminate of potash mordants the hardest drying does no injury. In other respects the aluminate is more delicate and sensitive than the acetate, more easily injured in the fixing, and more easily takes up impurities, organic or inorganic, from inferior qualities of water.

The nitrate and hydrochlorate of alumina are used to a small extent in steam colours, and in certain combinations the oxalate and tartrate of alumina occur.

Mordants of iron are of ancient use; the only one of special importance in calico printing is the acetate of iron, known generally as iron liquor, or black liquor. The first crude acetate of iron was probably made by steeping old iron in the sour acetous liquids derived from the fermentation of rice or flour: such mordants were used by the Hindoos. The making of iron liquor was patented in 1780 by Flight; he directs iron to be steeped in "water drawn from tar or tar oil, and the liquor mixed with starch, flour, or gum, to give blacks and purples;" by this water we may understand pyroligneous acid, and this process may be said to be the one used at the present day for making the best quality of iron mordant. Two years later, in 1782, Bootiman patented the method of steeping iron filings, iron hooks, or other thin iron, in a mixture of water with wheat, flour, barley, bran, or any other vegetable that will produce an acid when mixed with water, being practically the method used at earlier periods by native Indian printers. On the Continent iron liquor is yet made in certain parts from sour beer. No form of acetic acid seems so suitable as the pyroligneous for making iron liquor, if the acid does not contain too much non-volatile matter. The small amount of organic matter present appears to be useful in preventing the too rapid oxidation of the iron, which would be injurious for all delicate shades; hence the pyroligneous acid is preferable to pure acetic acid, for in the latter case it is found that dilute solutions are very easily oxidized and decomposed, the iron takes the form of the peroxide, and the solution loses available iron, or becomes very uncertain in its composition, and irregular in its results; while the pyrolignite keeps well, as it does not appear that the iron ever attains the maximum degree of oxidation.

Iron liquor is seldom made in any print works in Great Britain; it is found in commerce as a dark-coloured fluid, marking from 24° to 28° Tw. On the Continent it is to be found in a very concentrated syrupy state, about three times the strength of the ordinary home supply, perfectly miscible with water, and of excellent quality.

Iron liquor can be thickened with any of the usual thickenings of good quality, but its powers of fixing on fibre are very much weakened by the presence of any sugar or saccharine principles in the thickening; therefore wheaten flour, injured by heat and damp, or those gums and other thickenings made by means of acids, may be found to give very inferior results with diluted iron mordants.

No other iron mordant is used in calico printing; the sulphate and nitrate of iron are largely used in piece dyeing. The iron buff of the calico printers is very rarely used as a mordant; it is an acetate or sulpho-acetate of iron made from sulphate of iron and acetate of lead. For the topical application of extract of madder or alizarin purples or lilacs, although good results can be obtained from a fair quality of commercial iron liquor, the colour mixer will find it advantageous to prepare his own liquor from sulphate of iron and acetate of lime, or acetate of lead; the white acetate of lime being preferable, and used in slight excess, so as to have some acetate of lime in solution.

Tin mordants are very rarely used in calico printing in the way that iron and alumina mordants are used. The oxides and salts of tin do not belong to the same chemical group as those of alumina and iron, and though they possess strong affinities for both fibre and colouring matter, it has not hitherto been found possible to prepare any mordant of tin which can be thickened and applied to calico in the same way that the salts of the other two metals can be used for dyeing. An apparent exception to this statement is the so-called garancin orange, made from a salt of tin, an acetate, and decoction of Persian berries, which being printed along with other mordants, goes through the dunging and cleansing process, and is dyed up in garancin with them. In this case it might be supposed that an acetate of tin was acting as a real mordant, the same as the acetate of alumina, and producing a different shade of colour; but it is evident that the garancin orange is little more than a spirit yellow, which by care can be made to stand the garancin dye, and absorbing some red, yields an orange hue of but little stability compared with the other colours. When chloride of tin is added in moderate proportion to acetate of alumina mordant a complex reaction takes place, which is not fully understood; but the mixture has some of the properties of the chloride of tin, it can resist and even discharge iron mordants, while it dyes up good and full shades of red with madder and garancin. Upon analysis of the mordant remaining upon the cloth, a certain quantity of tin is found along with the alumina, forming a compound mordant, which is believed to have a greater affinity for colouring matter and fibre than either metal separately, because the mordant cannot be discharged completely by the same acids which would discharge an alumina mordant; but in point of fact it is the tin only which resists these acids. The alumina is easily dissolved out, and the amount of tin remaining is insufficient to dye up anything which can be properly called a colour. The powers which tin salt exercises in what are called resist reds is in great measure due to its deoxidizing powers, and converting a certain portion of the acetate into the muriate of alumina. If calico be prepared with chlorate of potash, as it is for some purposes, it will be found that a resist red, which is quite capable of throwing off purple covers when printed upon ordinary calico, fails to resist them when it is printed upon the prepared calico, and this clearly because the tin is raised by the chlorate to its maximum degree of oxidation.

Although salts of tin cannot be used in calico printing for dyeing, they are extensively used in steam colours as mordants, and are also largely employed in preparing or mordanting the whole surface of the calico previous to printing steam colours.

The chief compounds of tin in use are the crystals of tin, called also muriate of tin, chloride of tin, and stannous chloride; a solution of the same salt called liquid muriate of tin; the liquid bichloride of tin, stannic chloride, is not much used; the oxymuriate of tin, which is generally a mixture of the two chlorides, is used for spirit colours; and the stannate of soda, which is the principal salt used in preparing or mordanting cloth before printing.

The preparation of calico with tin is important for the majority of steam colours; it is simple and certain, if good materials and ordinary care are employed. The cloth is saturated with a solution of stannate of soda of a strength proportioned to the styles to be printed; it is then passed into dilute sulphuric acid, washed and dried. The points to be attended to are an even uniform impregnation of the stannate, a sufficient quantity of sulphuric acid, a gentle and not too hard drying after washing. Badly prepared cloth may be usually traced to an inferior quality of stannate, or to a deficient quantity or strength of sours. For styles requiring a very strong prepare the process of passing in stannate and acid may be repeated two or three times, the moisture of the cloth being as much as possible expressed between the treatments. For woollen mixed goods there are various methods of preparing. Some systems employ the stannate only, others the acid salts only; others again prepare in stannate, and then over again in bichloride or oxymuriate, the object being to deposit as great a quantity of oxide of tin upon the cloth as can possibly be retained by it.

The salts of chromium present much analogy in their chemical constitution to those of iron and alumina, and have been prepared as mordants; but until these few years past have had but a very restricted application, and even at the present time are scarcely ever used, except as constituents of steam colours. Although chrome alum is an article of commerce, and it could be employed in the same way as alumina alum to make the chromium mordants, the colour-mixer usually prefers to operate upon the bichromate of potash as the more convenient source of chromium for his purposes. The usual mordants of this metal in use are the acetate and nitrate, and they may be prepared by one of the following methods:—For acetate of chromium, 26

lbs. of bichromate are dissolved in 5 to 6 gallons of boiling water in an earthenware vessel, and 32 lbs. of strong sulphuric acid carefully added, then 6¼ lbs. of wheaten starch are added in small portions, so as to keep the effervescence within controllable limits; when the action is complete, and the liquor somewhat cooled, a solution of 50 lbs. of white sugar of lead in 5 gallons of hot water is well mixed with it, the sulphate of lead deposits, and the clear liquid floating above is the acetate of chromium.

Nitrate of chromium may be made as follows:—17 lbs. of bichromate dissolved in 2 gallons of boiling water, and 27½ lbs. of nitric acid added, then, by small portions, 5¼ lbs. of ordinary moist sugar, which has been previously dissolved in 1½ gallon of water. Upon cooling crystals of nitrate of potash will separate, and the clear liquor is the so-called nitrate of chromium.

Witz gives the following modification, which may be called the aceto-nitrate of chromium:—In an earthenware vessel 6 lbs. of bichromate in coarse powder are dissolved in 9 lbs. of boiling water and half a gallon of nitric acid at 36° B.; and then a mixture of 23 ounces measure of white glycerine, marking 28° B., and 8½ lbs. by measure of acetic acid at 7° B. are added slowly at first, but afterwards sufficiently quickly to maintain the heat of the reaction at a high point, otherwise the decomposition is incomplete, and the liquid will remain brown coloured. When the decomposition is finished the liquor is transferred to a pan and boiled for a few minutes, until a portion viewed in a thin layer has a beautiful green colour; it is then transferred to the pot and left all night to cool. A considerable crystallization of saltpetre takes place, the clear liquor is decanted, and the crystals washed with a little cold water, and the whole mordant brought to a strength of about 30° B. The samples of colours appended to the paper of Witz, in vol. i. of the *Bulletin of the Industrial Society of Rouen*, and obtained from this mordant with logwood, prussiate, berries, catechu, and alizarin, by steaming and soaping, are all excellent of their kind.

Other mordants than those enumerated are only employed for special styles and colours, and most of them will come under consideration when treating of the method of fixing mordants.

The only real mordants for general dyeing purposes in calico printing are the acetates of alumina and iron; these two compounds have been shown by Crum and other chemists to possess most curious and exceptional properties, which have no doubt important bearings upon their application as mordants. Crum showed that the acetate obtained by decomposing pure sulphate of alumina with acetate of lead was in all probability not a teracetate, resembling the sulphate in its constitution, but a mixture of biacetate of alumina with an atom of free acetic acid; upon quick but careful evaporation by regulated heat a residue of biacetate of alumina was obtained perfectly soluble in water. By boiling the acetate of alumina the whole of the alumina is deposited, combined with two-thirds of the acetic acid, the remaining third being left in the liquid. When the solution of the biacetate of alumina is exposed to heat for several days, it is seemingly split up into acetic acid and a modified alumina, which is soluble in water, but which is incapable of acting as a mordant; and when forced, as it were, to combine with colouring matters, it gives translucent lakes quite different from the dense opaque lakes which ordinary alumina gives with the same colouring matters. The peracetate of iron presents analogous properties, which, however, do not seem to extend to the protoacetate which is used by printers and dyers. These properties, and especially the existence of a modification of both alumina and iron, which do not act as mordants, may throw some light upon accidents in printing which from time to time occur and perplex the inexperienced colourist.

The practical precautions in printing acetate of alumina mordants are chiefly connected with the drying. If too quickly or too strongly heated in the drying, they are so much injured for dyeing good shades that no after care will succeed in obtaining full and saturated colours. This defect, which is less observed in strong reds and chocolates, is very conspicuous in light reds, and especially where the red liquor is for pale pinks, and reduced to a strength of less than 2° Tw. In such a case, if the temperature of the cloth reaches 212° Fahr. by actual contact with a metallic surface of that temperature, the deposition of the mordant becomes irregular, and only inferior results can be obtained in dyeing. To reduce the excessive sensitiveness of these dilute mordants, it is usual to employ a considerable excess of free acetic acid in the colour; and to provide against too much heating of the cloth, the steam chests are so arranged that the cloth shall not touch them, and sometimes the first range is further covered with cloth. In printing strongly acid alumina mordants care must be taken that the chests and rollers, which may be touched by the yet moist colours, are clean and free from iron rust or dust, which nearly always contains iron. It has happened in padding pink that a tinned iron roller at the top of a set of chests, the existence of which had been overlooked, was the cause of serious damage to the work by communicating iron to the cloth, which dyed up in specks of dark purple all over the piece. And on another occasion a lot of pad pinks were rendered inferior by the dust from the brushing down of an adjoining set of chests while the pads were being printed.

Iron mordants, even when very dilute, can be printed with much less risk of injury than alumina mordants; but as they are sometimes used so dilute as 1 of iron to 150 of water, it is evident that every attention must be paid to the state of the cloth, for very small causes would prevent the fixation of so feeble a solution. It is to guard against irregularities which might proceed from acid exhalations adhering to the cloth, or other resisting and destructive agents, that some of the best printers prepare all their cloth for pad purples with a preparation of

chlorate of potash, either with or without addition of alkaline arsenite or arseniate.

AGEING.—After the printing and drying the calico is submitted to what is called "ageing."

The method of ageing has passed through many phases, which are probably not yet complete. It was at an early period called stoveing, because the pieces after printing were hung up in rooms highly heated by means of stoves, and apparently without any provision for keeping the air moist. The usual process in England, until within the last few years, was to hang the goods up in rooms freely exposed to the currents of external air, and without any provision for either heating or moistening the air. Ageing under these conditions was slow and irregular; a period of three days and nights was thought necessary for light styles of covered purples; heavier work, as garancins, were not unfrequently hung up for a week or more. In the usual moist atmosphere and temperate climate of these countries, the only inconvenience of this system was the length of time required to be certain of the ageing. In the case of dry winds and frosty weather the ageing was retarded, and sometimes to such an extent, that the printing was stopped for days together until the accumulated goods were disposed of. The Alsatian printers appear to have been the first to introduce closed ageing rooms with an artificially moistened atmosphere, and the idea of continuous ageing is due to JOHN THOM of Birkacre, but then of Mayfield, who patented the machine in 1849; it was, however, not much used, except as a sulphuring machine, until WALTER CRUM of Thornliebank, some years later, worked out the process, and showed the conditions necessary to success.

The ageing machine, as usually constructed, is a room provided with a series of rollers above and below, by means of which the cloth to be aged

Fig. 16.

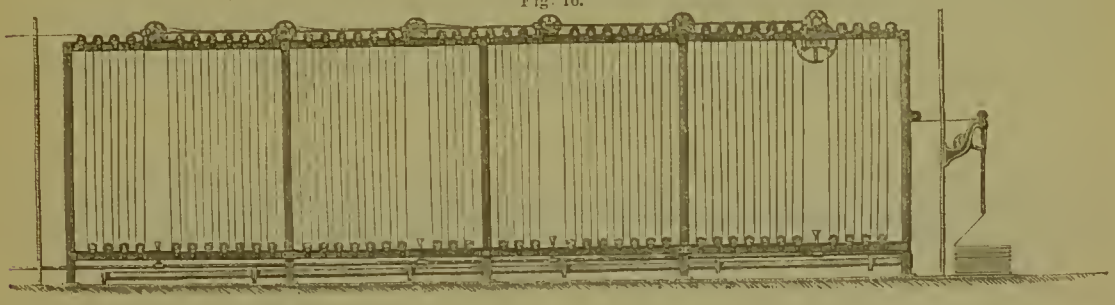
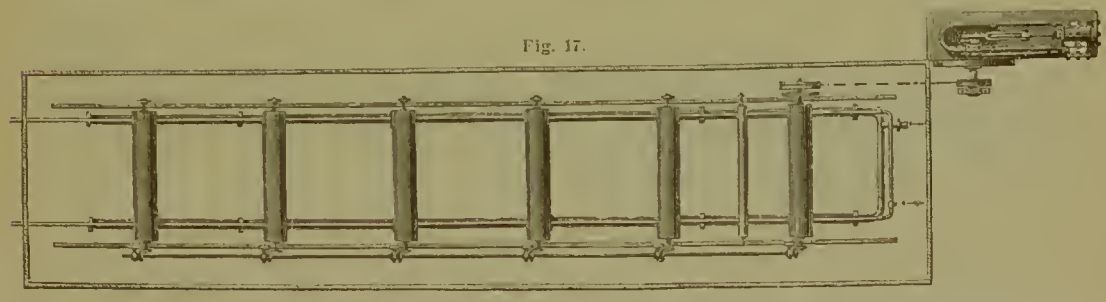


Fig. 17.



travels through, and is exposed to a warm and moist atmosphere. The form and dimensions of this room must vary according to the conveniences of the works; but it must be of such dimensions that a given portion of a piece shall be from fifteen to twenty-five minutes in traversing the room, and that the rate of delivery shall be rapid enough to meet the quantity of goods printed. Fig. 16 is a sectional elevation of an ageing machine, and Fig. 17 is a plan of an ageing machine.

The temperature of the air, and its degree of humidity, may vary within considerable limits without injury to the work; but the higher the temperature, and the more saturated the air, the more effective is the ageing. In practice, however, it is not found convenient to go higher than 100° Fahr. for the dry bulb thermometer; and if the wet bulb be at say 94° or 95°, the atmosphere is in a favourable state for rapid ageing. Temperatures of 20° lower than these may also be found suitable for lighter work, or even 20° or 30° higher may be used with advantage. Upon this point the local position of the machine is the only true guide. If in a warm place, as over the drying room of the machines, and surrounded by warm air, a higher temperature and a closer saturation can be employed; but in such situations the difficulty will be found to consist in keeping the atmosphere sufficiently moist. In other localities where the external atmosphere is not heated, it will be found necessary to work at comparatively low temperatures, on account of the danger of drops of water condensed from the steam either inside or outside the machine. The external indications of the machine working in a suitably warm and moist atmosphere, are in the soft feeling of the cloth as it is delivered at the exit, the amount of acetic acid evolved, and the development of colour as seen in catechu brown. An experienced

foreman can tell very well upon putting his face inside the machine whether it is in good working order or not; the condensation of moisture upon the skin, and the feel of the air on the lungs, are sufficient indications for him.

After having passed through the ageing machine, the pieces are bundled up and placed in a room kept warm and moist, and are left there for a night or longer before going on to the dye house, or before being passed a second time through the ageing machine.

The action of the warm and moist air upon the printed cloth, and upon the mordants, is in the first place to restore the water naturally existing in calico, which has been expelled by drying; then to bring the thickening into what may be called a normal state of moisture from the hard dried state in which it left the drying part of the printing machine; and then to commence a chemical action upon the mordants, which is partly an oxidation, and partly a decomposition. That there is oxidation direct or indirect (even from the air or from the constituents of the colour) is visible upon comparing cloth printed with catechu brown, iron buff, or aniline black, before and after passing through the machine; that there is decomposition of the acetates is apparent from the torrents of acetic acid liberated from heavy mordants of red or chocolate, which make it impossible to support the atmosphere at the upper part of the ageing machine. But it is highly probable that the useful action of the ageing machine is nearly all confined to giving a proper amount of moisture to the dried cloth and colours. It would not be safe to send out anything heavy direct from the ageing machine into the dye house; it is found beneficial in all cases, and necessary in some, to leave the printed cloth, as before mentioned, some hours longer in a proper atmosphere. CRUM held that the bundling up of the cloth did not interfere with the oxidation supposed to be necessary, for that the power of diffusion of gases was sufficient to maintain the necessary circulation, even when the cloth was pretty tightly wrapped up. The experience of practical men will hardly support this view, for in the rare cases where the action of oxidation is at all visible, it is evident that it is much more apparent on the exterior of the bundles and edges of the pieces. In such a colour as catechu brown, which may be said to carry a good deal of its required oxygen in the nitrate of copper, it is not very perceptible, except in heavy masses; it is plainly seen in strong iron buffs, or most of all in aniline black. If ageing was chiefly or entirely a matter of oxidation or of chemical action, the ageing machine would be a failure, for there is very little oxidation, and very little evolution of acetic acid, when the pieces have left the ageing machine. But it is supposed that the most essential action of ageing consists in putting the thickening into a soft or plastic state, and keeping it so for such a length of time as will enable the mordant to get into intimate contact with the fibre.

Although the ageing machine is very generally employed, still ageing by hanging is much practised, and found to be very safe, and sometimes more economical than the machine. For this purpose an artificially warmed and moistened atmosphere is nearly universally employed; to obtain a regular distribution of moistened air in large rooms is not difficult by means of jets of steam, but in confined spaces it requires some care.

The following is a simple and effective injection method:—A wooden pipe, about 9 inches square inside, and as long as the room, was laid down on the floor, or suspended against the wall; it was bored at intervals of a foot on one of its sides with holes an inch in diameter; one end of the pipe was closed, and a steam jet from a nozzle of one-eighth of an inch or less introduced at the open end, blowing in the direction of the length of the wooden pipe. The steam jet drew in a vast volume of air, which became thoroughly mixed with the steam, and was expelled with force from the lateral openings, which were so directed as not to make the current impinge upon the goods, but strike against the floor or ceiling. By having the open end of the wooden pipe outside the room fresh air and ventilation were secured, and by a large steam pipe inside the tube, or so placed that the air and steam passed over it, the necessary temperature was obtained. (O'NEILL.)

The temperature and degree of moisture in ageing rooms varies very much in different places. It is usual to keep the temperature so low that operatives can work in it without inconvenience; another method, which was much followed on the Continent, and with good results, consisted in filling the room with goods, say a thousand pieces or more, then closing it and turning on the steam both in the warming pipes and moistening jets, until the temperature reached 110° or 120° Fahr., and the air nearly saturated with moisture. The writer has been in such rooms for the few minutes it was possible to endure the temperature, and felt the pieces, which were quite soft, and seemed to threaten the running of the colours, which, however, he was told never happened. When the heating has gone on for some hours the jets of steam are turned off, the heating pipes being kept on, and after a while the room opened and the goods taken down.

Ageing machines have been constructed to work at temperatures of 150° to 170° Fahr., and have been found to answer very well for garancin styles, but generally to finish the ageing after the pieces had been hung a day or two. To keep up this high temperature, and to prevent drops of water, it is necessary to have the ceiling of such a machine composed of steam chests; the time of exposure may be reduced to three or four minutes, and consequently smaller machines are made than the usual low temperature machines.

The use of chemical gases to assist ageing has given no good practical results. In those cases where ammonia gas is employed the action cannot be properly compared with ageing; it is more correctly a fixing or a neutralizing action, and generally follows the ageing correctly so called.

Ageing liquors made from chlorate of potash and

alkaline arsenites have been used to assist the fixing of black and chocolate mordants; they are mixed with the colour, and are somewhat uncertain and capricious in their action.

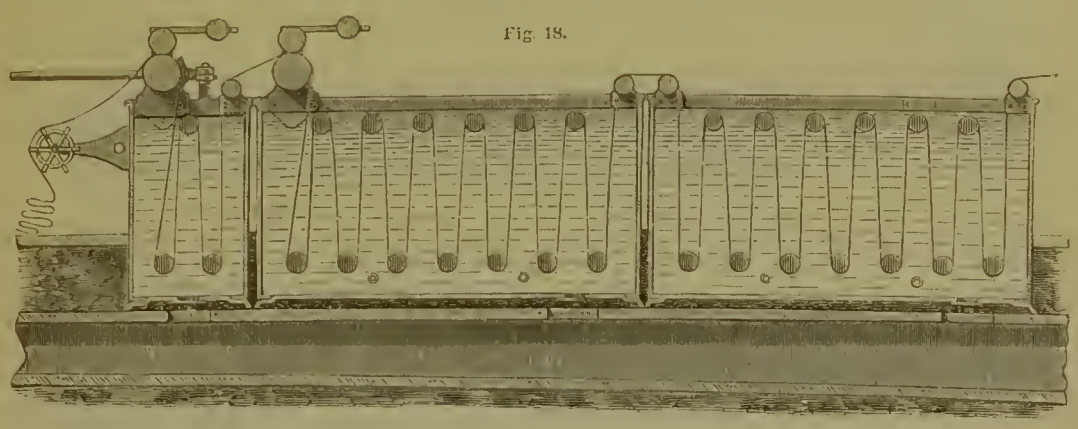
Dunging and Fixing.—The ageing is followed by the process called dunging, cleansing, or fixing.

The dunging process is carried out in quadrangular vessels preferably made of cast iron, which are furnished with rollers above and below, some of which are driven by power. It is usual to have a series of three vessels or dunging dollies, and at the end of each a wince or draw rollers driven by power to draw the pieces through the liquid, the pieces having been previously sewn together.

Fig. 18 shows two of the three cisterns or dollies of the first dunging arrangement; the cloth proceeds from right to left, and is made finally to pass through a small cistern of cold water, and is then taken off by the wince either to go on directly to the second dunging or to be washed.

The substance which has been used from time immemorial in this process is cow dung, and although several effective substitutes have been found it is still much used, and for some purposes preferred by intelligent dyers. It is only a matter of conjecture as to what portion of the cow dung acts usefully, and what the action is upon the mordants; this excrement is of a very complex nature, and chemists have not succeeded in their attempts to define the constituents upon which its efficacy as a cleansing or fixing agent depend. Practically it is found that if the pieces after ageing were passed into unmixed water, warm or cold, the colours after dyeing would not be full or saturated, and the whites would be very bad after a few pieces had been passed through the vessel of hot or cold water; both these effects being due to the fact that no practicable agency can fix the whole of the mordants printed on calico, that on passing through water the unfixed mordant dissolves in it, and that after a while the water is converted into a dilute mordant, which fixes more or less completely over the whole surface, spoiling both whites and colours. If thoroughly aged cloth be washed off after printing in a running stream, where the water in contact with the cloth is perpetually renewed, the inconveniences described above are

Fig. 18.



reduced to a minimum, and fair work can be produced; so that it might be said that the use of cow dung and substitutes is to enable the dyer to wash off a great quantity of mordanted cloth in a limited quantity of water without injuring the colours.

Supposing that cow dung is the substance used, the procedure is as follows: the dunging cistern is filled with water to the height of the top rollers, the steam is turned on, and while the water is heating a quantity of cow dung is stirred up in it; this quantity varies according to the nature of the dung, and the styles to be dunged, from 1 to 5 per cent. of the quantity of water. The temperature of dunging is regulated by the styles; light styles and light colours require only a low temperature, say about 140° Fahr. Alumina mordants for pink, and especially for bark yellows, should be dunged at as low a temperature as will suffice to dissolve out the thickening; for yellows, in the neutral style, to be dyed in bark, and for red liquor pinks from madder, where there is not much colour, washing off in cold water in a stream without dunging is the best preparation for dyeing. For dark styles printed with paste colours, as the usual garancin styles, and for styles containing much acid, a high temperature, say 180° Fahr., is required; and it is useful, and may be necessary, to add a few pounds of ground chalk to each of the dunging cisterns, especially for patterns with acid in. This refers to the first dunging, into which the pieces go at full width, and which occupies from one to three minutes. The dung and chalk are kept up to the first strength by additions made at stated intervals of time, or according to the number of pieces passed through.

Fig. 19 shows one of the second dunging becks, of which there may be three or more side by side; the cloth no longer at full width, but as dyers say in the rope, passes in a spiral manner continuously and without interruption through the whole series, and is then washed.

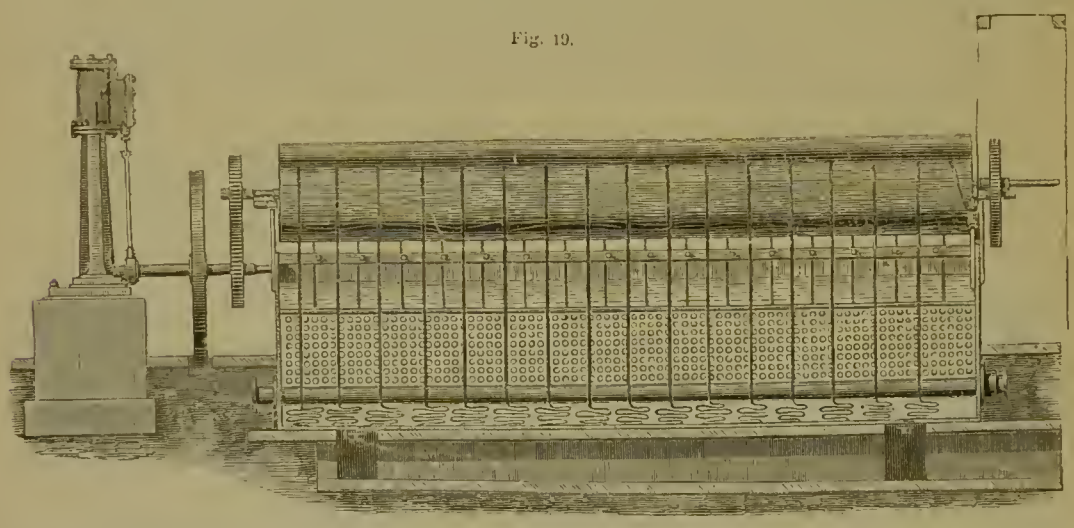
Dyers are divided in opinion as to whether the goods should be washed between the first and second dunging or not. If the washing machine be conveniently placed, this does not involve much trouble or expense, and it keeps the second dung becks clean for a longer time; but in the majority of styles there seems to be no necessity for it, and it is better even that the pieces from the first dunging should

not be cooled by passing through cold water, but that they should go straight on, hot as they are, into the second dunging.

The effect of the first dunging is to dissolve off the more soluble matters in the colours or mordants. Most of the unfixed oxides are removed, and held in such a state of solution or suspension in the dung liquor as not to be hurtful to other mordants and the whites; but the action is incomplete, and the greater portion of the starch or flour thickening is not dissolved off, and a good deal of unfixed mordant is still mechanically adhering by means of this unremoved thickening. The object of the second dunging is to complete the cleansing of the cloth from these matters. The temperature of the second dunging must also vary with the styles. Generally paste thickenings must have a high temperature, but not exceeding 170° Fahr.; iron mordants and chocolate mordants, containing a large proportion of iron, seem to be uninjured even by an excessive amount of dunging. It is not so with alumina mordants, which are seriously affected if the strength of dung, temperature, or time, pass a certain given limit, and these styles demand a close attention on the part of the dyer.

The main object of dunging, it is seen, is to remove the thickening matters employed by the colour-mixer; with them the unfixed mordant comes away, and the cloth goes into the dye beck clean, without any loose mordants which may be detached in the dyeing process, and cause trouble and irregularity in the dye beck. The complete removal of some paste thickenings is nearly impossible. They may be repeatedly dunged and washed, and upon drying a fent it is found still stiff with thickening, and if tested by iodine in the laboratory the presence of starch is readily detected. If inferior work is the consequence the dyer cannot be justly blamed; the fault is either in the quality of the thickening used, or in a baking of the prints on the steam chests of the drying machine. In case of such a difficulty, the experienced dyer will give the longest dunging and

Fig. 19.



the best washings that the styles will support, and if possible leave the goods wet all night, and wash again before entering into the dye, and so mitigate as much as possible the inferiority which is inevitable. For in the course of the two hours time the goods are running, say in garancin, alizarin, or madder, the obstinate thickening is gradually giving way and being dissolved in the beck. The mordant which it has held becomes diffused in the dye liquor, and absorbs the colouring element which ought to be reserved solely for the design, and unless an excess of colouring matter has been used the goods are under-dyed; the beck liquor, which ought to be clear, is highly coloured and opaque, and first-class work cannot be obtained. Twenty minutes to half an hour is the longest time that should be required in the second dunging, and this is followed by two, three, or four passages through the washing machine. The practical test of a well-dunged cloth is to take an end and rub or beat it in the hand, and squeeze out the water. If the water comes clean, the presumption is that the cloth is well dunged and washed. The disappearance of the sightening is not a reliable guide. In some cases of dunging with substitutes the logwood sightening of red liquor mordants dissolves out, and dyes the whole piece of a light slate colour; but no harm was ever known to follow this appearance.

There have been a great number of chemical preparations used as substitutes for cow dung, but only two are of sufficient importance to require mentioning, and these are the arseniate and the silicate of soda.

The solution of arseniate of soda, made at about 28° Tw., may be used in proportions of 1 part to 100 of water for the strongest dunging liquor, and 1 to 300 of water for the weakest, adding chalk for most styles. When of good quality the arseniate is a perfect substitute for cow dung, and much more reliable and more pleasant to work with. The writer was at one time so placed that cow dung could not be got without great expense and difficulty, and for three years employed nothing but arseniate of soda, and with perfectly satisfactory results. The

only point in which it yielded to cow dung seemed to be in the finer shades of madder pink, which after experience showed could be obtained of a purer and fuller tone with cow dung. Alumina mordants are, so to speak, blackened by the arseniate, and if a piece containing red be dunged in cow's dung, and another piece of the same printing, but dunged in arseniate, be dyed together, the latter is found to be much slower in absorbing colour, requires a higher temperature, and is never quite so fully saturated as the cow-dunged sample. For iron mordants and for chocolates the arseniate is at least not inferior to cow dung. Many dyers who use arseniate consider they could not succeed with it unless a certain mixture of cow dung was mixed in the cisterns and becks along with it. Such a mixture, although not injurious, is quite unnecessary with good thickenings. It may serve a useful purpose in helping to scour off thickenings by friction of its insoluble matters, but as a chemical agent it is entirely eclipsed by the arseniate.

Arseniate of soda is of variable quality, and some qualities are quite unfit for dunging. The binarseniate is acid, and should be neutralized before using; the dyer generally uses chalk; caustic soda would be preferable if there were no risk of using an excess. The ordinary arseniate is sometimes sent out strongly alkaline; this is a great fault, and may lead to the damage of goods. A case came under the writer's observation, when fifty or sixty pieces of pinks were utterly spoiled by using an alkaline arseniate. The lightest pink was dissolved almost completely out, and the others seriously injured and of a very bad shade, and this although the temperature of the dunging was not higher than 120° Fahr. Upon discovery of the cause the alkaline arseniate was rectified by adding sulphuric acid, and then gave the usual good results.

The silicate of soda, though not a favourite in Great Britain, may be said to be the chief dung substitute employed on the Continent, and it is used successfully for all styles. It is made of very good quality, quite without free alkali, and is safe for the most delicate pinks, as well as purples and heavier colours. Common makes of silicate contain almost invariably free caustic or carbonate of soda, which act upon alumina mordants very powerfully and destructively, and cannot be safely used as dung substitutes.

In treating of cow dung nothing was said upon the fixing properties which it is supposed to possess. If it does actually enjoy the power of fixing or precipitating any unfixed mordant upon the fibre, it is only to a very small extent. But this is not the case with the two substitutes mentioned, which can be made into real fixing agents; that is, they can decompose such salts as acetate of iron or sulphate of alumina, with abstraction of their acids and precipitation of their bases, combined with the arsenic and silicic acids. The degree of dilution in which these salts are employed as dung substitutes renders it very doubtful whether they do exercise any fixing or precipitation of oxide upon the fibre or not; probably all their action is confined to making insoluble, and therefore inert, all the possible soluble oxides remaining after ageing. It is thought by many that that portion of the salts of iron or alumina which has not been fixed by a proper ageing had better not be fixed in the dunging process, which should be limited to a cleansing action.

*Fixing.*—Here it is proper to notice various operations of real fixing of mordants and colours, which are carried on in the same or similar apparatus as dunging, and at the same stage of the progress of the piece; such are fixing lead for orange, iron buffs, aniline blacks, and generally what are often called soda colours and chromed shades. Without entering into details of the various styles a description of the fixing agents would hardly be intelligible, the object generally being to precipitate the mordanting salt or colouring oxide upon the cloth by decomposing the salt with some powerful agent. For example, to obtain a chrome orange a thickened solution of acetate and nitrate of lead is printed, and may be submitted to the ageing process, but neither of these lead salts undergo any chemical change by ageing, nor show any affinity for the fibre, and would be almost entirely washed away if passed through any of the dunging solutions or substitutes. The cloth must be passed into a fixing liquor, which may be either a strong and hot solution of sulphate of soda or a cold and moderately strong mixture of sulphuric acid with water; the soluble lead salts are completely changed into the insoluble sulphate, which adheres to the cloth and is a real mordant, to be dyed up by a real colouring matter, the chromic acid in bichromate of potash. In the case of iron buff, which is usually a mixture of acetate and sulphate of iron, a portion of the iron is fixed by ageing and a portion not. To complete the fixing the cloth is passed through lime and water, through solution of soda ash, or through dilute caustic soda, and the depth of shade obtained is proportioned to the strength and activity of the fixing solution: so with other metallic colours, as manganese, chromium, &c. This is often called raising the colour, and is applied with many modifications to the various classes of colours requiring it; and, as before stated, the operation is carried out exactly like the first dunging of the usual dyed styles.

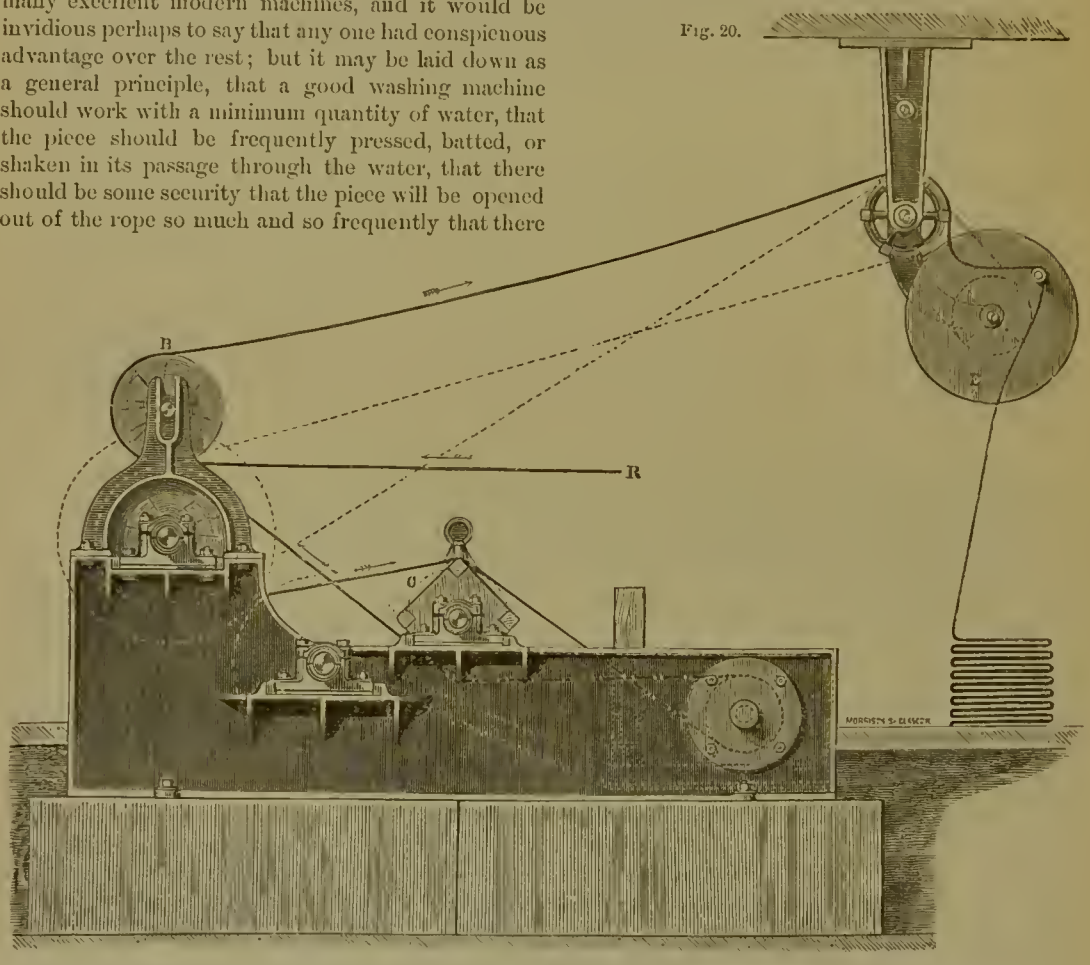
*Washing.*—Washing after dunging is a very important step which is often neglected, to the great injury of the colours. In dunging with cow dung, the absence of visible remains of the dung on the piece was taken as a test of sufficient washing; but with the substitutes there is no similar test, and the dyer must use other means of ascertaining whether justice has been done in this respect. Defective washing in modern washing machines may be generally traced either to want of a sufficient supply of water, or to the cloth being so tight that some parts of it never get into free contact with the water.

Washing in earlier times, and even yet in some places, was effected in running streams, and various machines have been devised to supplant hand labour in drawing the goods through the water, and giving them

such a degree of pressure and friction as will best facilitate the removal of adhering matters. But most dyers have to work with a limited supply of water. Of all the washing machines ever used, probably none excelled the dash wheel for efficiency, and it was the principal machine in use up to about 1856, when it began to yield to more rapid methods of washing. The drawback to the dash wheel was its slowness, the large quantity of water it required, and the great power it took to drive. There are many excellent modern machines, and it would be invidious perhaps to say that any one had conspicuous advantage over the rest; but it may be laid down as a general principle, that a good washing machine should work with a minimum quantity of water, that the piece should be frequently pressed, batted, or shaken in its passage through the water, that there should be some security that the piece will be opened out of the rope so much and so frequently that there is reasonable certainty that every part of it will be exposed to the washing action, and that the supply of water should be so arranged that the clean water comes in where the piece goes out, and that in the body of the machine the dirty water shall not mix with the cleaner. In addition to these practical requirements, it must be of such a construction as not to be liable to strain or tear the pieces, and not require too much power to drive it.

Figs. 20 and 21 show the end and sectional elevation

Fig. 20.



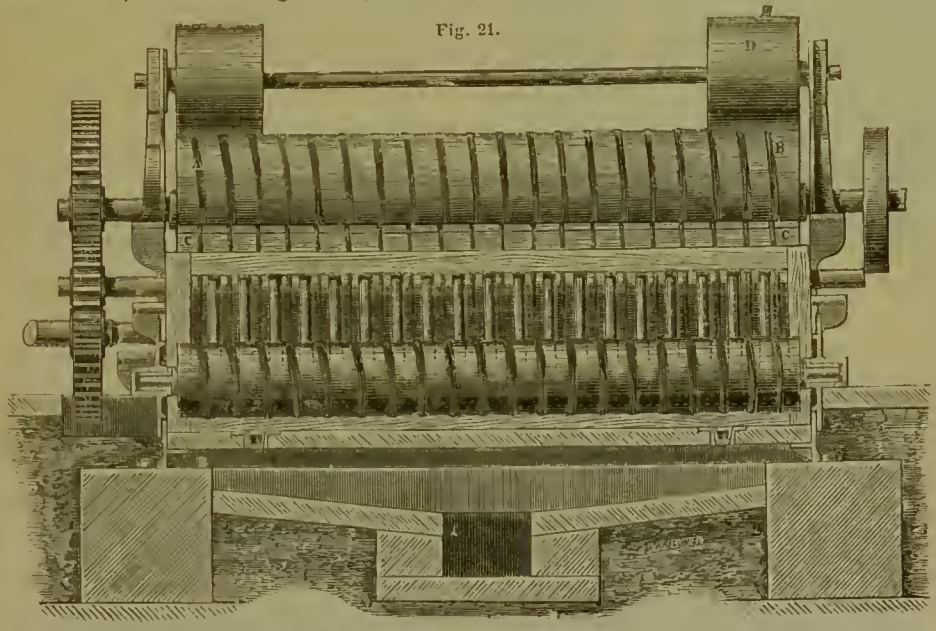

of a washing machine by Gadd of Manchester, which is well suited for dyehouse requirements. The cloth enters at R between the rollers, and travels in the direction of the arrow to *a*, where it passes over the square beater, and under the water supply from a perforated pipe, thence round a roller working under water, and back by the lower part of the square beater between the rollers A and C, and so spirally progressing until it is delivered by B and D, the latter being a pressure bowl to the plaiter down, E. The action of the square beater is to dash the cloth quickly and forcibly against the surface of the water, to keep it open, and by this mechanical movement detach matters which ought to be removed.

Dyeing Apparatus.—The cloth is now supposed to be ready for dyeing, it may be in madder, artificial alizarin, logwood, garancin, or other dyestuff, for the general procedure is the same in all cases.

The primitive system of dyeing was in copper pans heated by naked fire, and provided with a roller and winch at the top for keeping the goods in movement. From this old method, now only used in remote places and for some kinds of woollen dyeing, there have come down some trade terms yet heard in dyehouses—a dyer was a copper man, the process of dyeing was coppering, and stains which became visible in dyeing were copper stains. The application of jets of steam to heat the dyeing vessel instead of fire was made in England early in the present century, and the use of wooden dye becks soon followed, which could be constructed of a more convenient shape than copper pans, and were much less expensive. The first wooden dye becks were,

however, nothing more than oblong tubs, strongly made and coopered, with a wince sometimes for hand turning, which was gradually improved into driving by power. Perhaps the next improvement was in making the beck ends of cast iron, and soon afterwards the whole dye beck was made in a single casting of iron, and that material is now preferred. Lately attempts have been made to introduce dye becks of double cased copper, so that the dye liquid may be heated like the contents of a colour pan, without coming into contact with the steam, and so avoid the inconveniences which may arise from the impurity of the steam, or the increase of bulk due to its condensation in the dye beck. This principle of a dye beck, which had been long previously employed for yarns, was expected to have great advantages in madder dyeing, and generally in all cases of dyeing where the proper extraction or transfer of the colouring matter required a long continued beating of from two to three hours; for it was ingeniously argued that as the dyeing progressed, the amount of colouring matter diminished, and the volume of water increased, making it more and more difficult for the mordants to exhaust the dyestuff, whereas, in a rational system of dyeing, the volume of water should diminish in a ratio approximative to the diminishing quantity of colouring matter which remained to be extracted. The writer confesses he was very much disappointed after having advised a set of four of these becks to be put up at a very heavy cost, that he could not get the slightest advantage in the way of economizing dyestuff by their use. Hundreds of comparative trials were made with negative results, not only with madder, garancin, and alizarin, but also with logwood and bark; and it seemed to be clearly demonstrated that heating with naked steam was the best when proper arrangements of steam pipes were employed, and care taken that condensed water from the pipes did not enter the dye beck. The amount of steam required to beat one of the

Fig. 21.



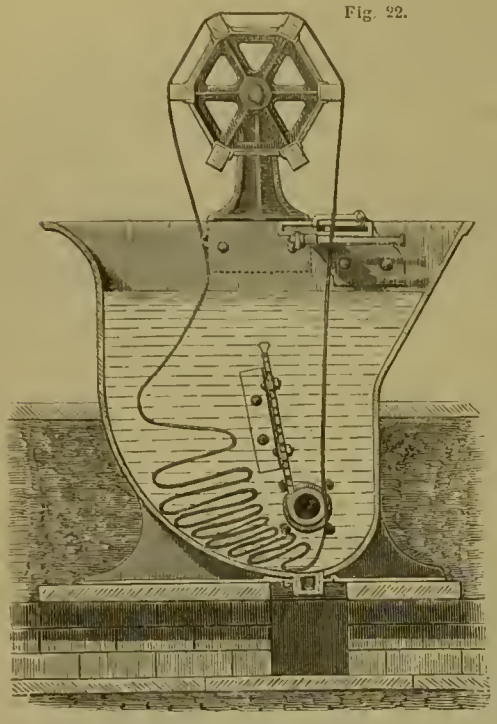

double-bottomed becks not clothed with any non-conducting substance was immensely more than was necessary for the common becks. Pieces run on these becks remarkably smoothly without any midfeather, until the beck is brought near the boil, when the absence of rail or roller at the bottom is felt.

Fig. 22 shows the end section of a cast-iron dye beck for madder dyeing, heated by naked steam supplied by perforations in a pipe extending the whole length of the beck. Fig. 23 shows a front sectional elevation of a dye beck on the continuous system, in which the pieces are all sewn together and run spirally.

The shape of the dye beck is devised so as to permit the dyeing of the pieces with the smallest possible quantity of liquid, which is important, in order to permit the mordants to exercise their attractive powers, and to avoid waste of steam, or heat up an unnecessary quantity of water. The system of spiral dyeing, or as it is sometimes called continuous dyeing, was introduced by Thompson in 1852. The pieces, sewn in one length, are entered at one end of the beck, and the slack being divided as equally as possible, the piece is gradually advanced towards the other end by means of the peg rails in a screw-like spiral progression, and the two extremities of the length of cloth being joined, the piece, when it has travelled the whole length of the beck, is drawn to the entering end over rollers guided by pot eyes, and repeats the same course. Thompson's plan included a cylindrical wince and a top-pressing roller, much the same as the modern continuous soap becks. It did not come into general use, because the operative dyers objected to its difficult management, and it was further believed that the smooth wince and smooth roller pressed the dyestuff into the cloth in a manner which was injurious to both colours and whites. At the present time the top pressing roller is dispensed with, and substituted by a pulley at each end of the wince, which enables the wince to be made

of the usual angular form, avoiding the constant squeezing of the piece and the necessity of a stripping roller, which all round winces require in slack dyeing.

Fig. 22.



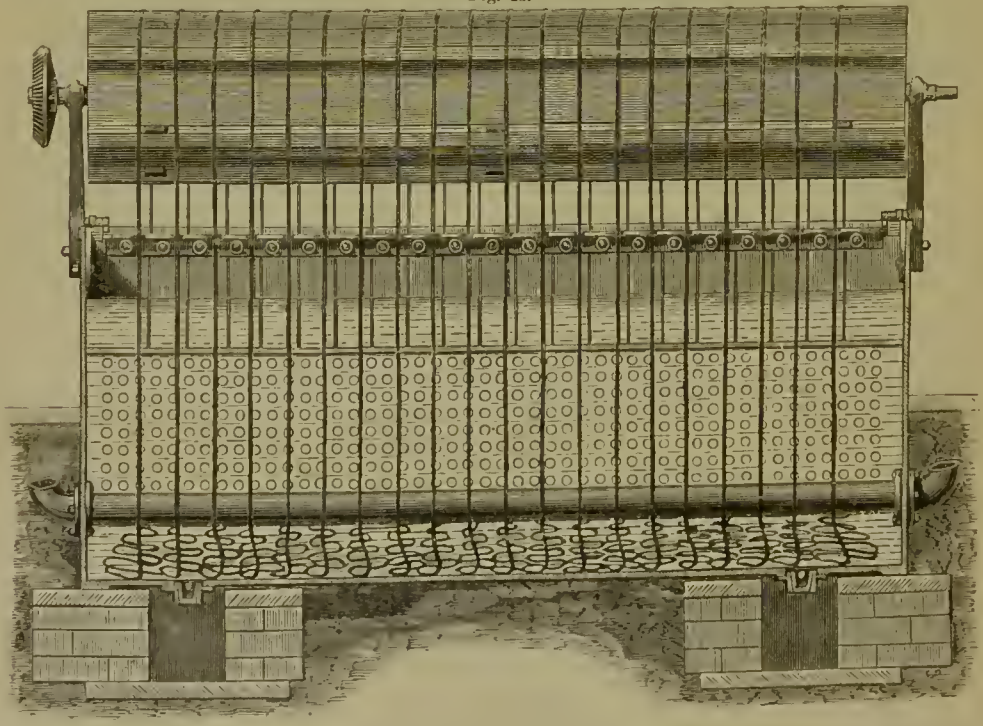
The spiral system insures regularity in the dyeing in so far as it secures uniformity of heating; in dye becks of an inferior construction there is a great liability of one end being much hotter than another, or of both ends being hotter than the middle, and the pieces which occupy these places are, of course, unequally dyed. In the spiral system, even if this defect exists, it cannot injure the work, because the pieces have an equal exposure to the liquid in every part of the beck, and must in this respect be all alike.

Since the introduction of concentrated extracts of madder and artificial alizarin, attempts have been made to dye the old madder styles in an apparatus analogous to the dunging dolly, sending the pieces through in the open state, and employing a large excess of colouring matter. By these means the time of dyeing may be reduced from two hours down to five minutes; but it does not appear that this plan is economically practicable, on account of injury and waste of the colouring matter, which more than counterbalance the saving in time.

The most ordinary method of dyeing for calico printing is to enter the pieces into the dye beck, either in a number of single lengths or spirally, and while they are running over the wince the dyestuff is added to the water; the steam is turned gradually on, and the heating carried on in a regular progressive manner without stopping, until it is supposed the pieces are sufficiently dyed, or the dyestuff exhausted. The time and temperature required to accomplish this vary for different styles, and for different dyestuffs.

Madder Dyeing.—In describing dyeing for calico printing, it was formerly necessary to consider it specially with regard to madder dyeing, that branch being far more important than all others, and the one most difficult and complicated. But the last

Fig. 23.



five years have witnessed the introduction and extension of the application of artificial alizarine, which has so far supplanted madder, that establishments which formerly consumed two tons of madder roots per day in the dye house, have now either entirely ceased to use it or employ it in very few cases of dyeing. All the history and analyses of the proximate principles of madder root, which have occupied many celebrated chemists, as SCHUNCK, DEBUS, ROCHLEDER, HIGGINS, KUHLMANN, STRECKER, and others, and which were supposed to be in some way or other connected with its colouring matter, and to influence its application in the arts, have lost their interest to the technical man. Rubian, erythrozym, and xanthin, with a score of other bodies, may or may not exist in this or that sample of madder root, or may or not be the cause of colouring matter in the madder; that is now a question of remote scientific interest. What is certain is that anthracene can be transformed into alizarin, and the successive steps of the transformation can be followed as clearly, as easily, and as certainly, as if we were going through a simple equation in algebra; and we come across none of the twenty or thirty subsidiary madder products which ingenious chemists formerly tried to connect together by linking them with alizarin.

The revolution effected by the introduction of artificial alizarin has been much more complete upon the Continent than in this country. Here the dye house is still occupied, though the dyeing product be an artificially made fluid or paste, and not the natural root of a plant; but abroad the madder dye house has no more dyeing to do, the colours are all applied topically and steamed, and there only remains washing and soaping to be completed after the old system. Whether madder dyeing is to be succeeded by alizarin dyeing as carried out in England, or by making a topical colour of it and fixing by steaming as on the Continent, is a question that cannot yet be answered, and the solution of which will in great measure depend upon economical considerations. This much is certain, however, that the Continental colourists have already arrived at a degree of perfection in the topical application of these colours in plate pinks, pad pinks, dark reds, lilac shirtings, and covered purples, which is scarcely credited by the English printer, and with which he can barely compete either in price or quality.

In the present state of affairs the purpose of this article will be best fulfilled by treating here of madder and alizarin colours together, whether the latter are obtained by dyeing or by steaming, for it will be found that the principles involved, and in fact many of the treatments, are identical or very similar.

Madder styles may require from a ½ lb. to 7 lbs. or 8 lbs of the root for the average piece, having from 6 lbs. to 7 lbs. weight of cotton; the smaller quantity is for the lighter styles of purple, with very little colour on the design, and the heavier for pink designs well covered, or pad pinks. There are various qualities of madder possessing different amounts of colouring matter. The French, Dutch, and Turkey madders do not differ greatly in tinctorial power, though having some distinctive properties; the Derbent or Caucasian madder is nearly twice as strong as the average quality of French, but it is rarely employed in this country. Derived from madder we have also garancin, garanceux, the so-called commercial alizarin, and lastly, the flowers of madder. They have all the same colouring principle, and their history and chemical properties are given in another place. They are mentioned now to state that the process of dyeing is the same for all; the subsequent treatments differ, but their behaviour in the dye beck is subject to the same general rules, and requires the same precautions and treatments. The artificial alizarin may also be included in the list.

The amount of water employed in the dye beck is to be the smallest quantity necessary for the proper circulation of the calico; there must be sufficient for the goods to move easily, and to hold the dyestuff in suspension, without any approach to thickness. An excess of water is against the dyeing, and to be avoided, because no water is so pure as not to contain some salts which are of an injurious tendency, and great dilution wastes colouring matter. In those styles which require more than 5 lbs. of madder per piece it is best to dye at twice, on account of the gelatinous state the liquor is likely to assume when there is too much madder in it; taking about three-fifths of the required quantity of madder for the first dyeing and the remainder for the second. The results in heavy reds and pinks is more regular than if the dyeing be attempted at one operation.

The heating of the beck is to be as regular as possible, never letting the temperature descend from a point once reached. Allusion has been made to the unequal heating of becks; this is owing to a bad arrangement of the steam pipes, or to the holes from which the steam issues in the beck being too large; irregularities may also happen from the becks not being set level in their foundations, and one end being deeper in water than the other.

The temperature for madder dyeing may be quickly raised to about 120° Fahr., and then gradually advanced to the temperature determined upon. For the usual run of work the time is two hours, and the highest temperature about 180° to 200°; for fine reds and pinks it is not desirable to go higher than 170°, and the time may be increased to three hours; for fine purples the temperature should not pass 180°. Garancin styles, with chocolate red and black, may be advantageously heated to the boiling point for the last half hour.

The points that the dyer has to attend to in the running of the pieces are merely mechanical, and the only accidents proper to the dye beck are torn pieces and turned threads, which may result from a stoppage of the circulation of the pieces, and the dragging of the wince against the stationary cloth. Turned threads, or as they are sometimes called "screeves," show most plainly upon padded or close covered styles, the printed side of the warp having been so pulled and twisted as to turn it out of its position on

the cloth, and to show the back or unprinted side on the face. This fault may happen after dyeing, in soaping, or even in washing, and is not necessarily due to the dyer's negligence. If pieces stand in the beck through any stoppage while the steam is blowing freely against the cloth, light places will often be observed. Pieces near the side of the beck are sometimes badly stained; this may be owing to impurities brought in with the steam. The presence of much condensed water in the steam pipes, which finds its way into the dye beck, is frequently a cause of inferior results in madder dyeing.

The dyeing being completed, the pieces are taken out either into a waggon to go to the washing machine, or placed upon a stillage from which the washing machine can draw them; or as was formerly usual, they are taken direct from the dye beck into a pit of cold water, where they are turned once or twice by the wince, to rinse and cool them, and thence to the washing machine.

The washing after dyeing may be effected in the same machine as was used after dunging. It is advisable to wash well, even for work which has to be soaped; and for garancin and similar styles which are not submitted to the soaping process, the washing must be of a very complete nature, and may require three or more passages through the washing machine. When the washing is completed, the cloth ought not to give any coloured liquor when a portion is rubbed in the hands, and the water wrung out.

For some kinds of work no more dye-house treatment is required, but for a good class of work even in garancins, alizarins, and logwood blacks, it is usual to pass the pieces through hot water and give another light wash. This is found beneficial, because the best washing in cold water leaves a hurtful amount of loose colouring matters or dye wood embedded in the fibres, which is either dissolved out or loosened by hot water and a slight subsequent washing.

All styles of madder and artificial alizarin work require further treatments in order to clear the white parts of the design, and to brighten and improve the colour.

Madder purples are now usually submitted in the first place to a passage through cold and very dilute solution of bleaching powder, so weak that it can scarcely be perceived by tasting. This passage may last from five to ten minutes, and is best done in a beck working on the spiral system, the cloth entering at one end and going through to the other, and then passed through a beck of clean water, which gives a sufficient amount of washing.

The soaping of madder styles is a very important operation, for upon it depends in a high degree the beauty and permanency of the colour, and the brightness of the white. The kind of soap to be used is one which should not contain anything but fatty matter, alkali, and water; a certain percentage of rosin is not disadvantageous, but a soap free from rosin is on the whole to be preferred, as that alone can be relied upon for the best quality of work. There are a great variety of soaps in use by printers, which show considerable differences of composition in analysis even of those kinds which are known to be good. It does not seem to be important what kind of fatty matter is employed, so that the fat is well combined with the alkali; and upon the whole, it appears that a slight excess of alkali, above that required to form a neutral soap, is an advantage. The pure curd soaps do not work well nor economically in average qualities of water; to use a dyer's term, they break too easily, and do not lather sufficiently. The best printers prefer a palm oil soap made from the unbleached oil, and entirely free from rosin or silicate of soda, and with an amount of alkali very slightly over the amount indicated by theory. But very good soaps are made from cheap fats, as bone tallow, oleine, and vegetable oils, and they have generally an advantage in being of a soft nature, and readily soluble in water. Many of the varieties of printers' soaps are sold in a highly hydrated state, and containing saline matters of an entirely useless character, and though offered at a low price, prove in practice less economical than higher priced and purer qualities. The action of soap upon madder work may be considered to be of two different kinds—there is the scouring and cleansing action to remove the impurities and the false dye principles which have fixed upon the mordants, and which hide or disguise the true colour; for this probably a very inferior quality of soap might suffice: the second action is of a more obscure and perhaps questionable nature; it consists in the appropriation by the mordant of a certain amount of fatty matter from the soap, and the retention and incorporation of it as an essential constituent of the colouring compound which is to remain upon the cloth. To fulfil the latter function, it is evident to the chemist that the soap employed must be of a very neutral nature, and nicely balanced in its proportion of fatty acid and alkali; for if it is demonstrated that in such a colour as madder red, as it exists in a finished print, there is found a definite proportion of fatty acid, and that this fatty acid is an essential constituent of the colour, it is clear that the dyer cannot hope to succeed in forming such a combination from inferior or badly made soaps, and therefore cannot hope to produce the best kind of colour.

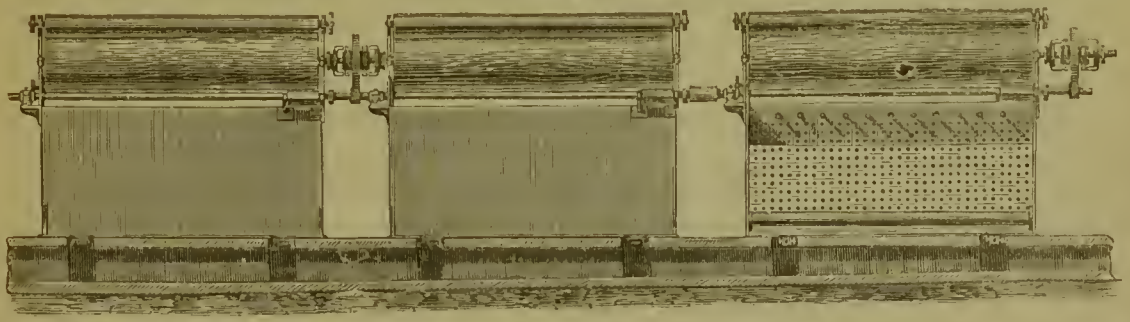
Purples and lilacs of the best quality can be obtained from several madder products without the use of soap, although soaped work has a softer and better appearance; but for madder reds and pinks, or with alizarin, the use of soap seems up to the present time a matter of absolute necessity, and it is quite certain that full and strong reds do actually absorb a large proportion of fatty matter from the soap; so much so that highly-soaped reds may be observed to mark off in steaming, and the marking has a decidedly greasy character; and the presence of fatty matter in the colour can be proved to demonstration, while the uncoloured parts of the print have at most absorbed a very trifling amount of it.

The modern system of soaping madder work is in

a series of connected becks, six or eight in number; they are similar in the body to dye becks, but the angular wince is replaced by a cylindrical solid or hollow wooden bowl, provided with a smaller pressing roller at top, and a stripping wince below to take the cloth off the large bowl, to which it has a tendency to adhere. The cloth is entered at the first beck, and progresses in a spiral manner through the whole series; the last beck may be in connection with a washing machine. There are many modifications in details of the continuous soaping arrangement, but most of them are of too minute a nature to need entering upon. The chief difficulty in working is when soaping at or near the boiling point; then the pieces are very subject to become entangled, and come up in "lumps," interrupting in a very annoying manner the progress of the work. The best mechanical arrangement to avoid this inconvenience is to have several mid-feathers in the beck, so as to keep the pieces as much as possible under their proper peg-rails; having the draw-rollers fixed at a height of say 3 feet or more above the level of the fluid is also a great assistance, for the greater the distance between the beck-level and the nip, so much more the chance of knots and folds shaking themselves free before they arrive at the nip; there is of course a loss of heat by the pieces passing through the cold air, but that is amply compensated for by ease and regularity in working. The inclination of the holes and depth of the steam pipe also influence the running of the pieces; the pipe should be as high in the liquid as it can be safely placed, and the direction of the steam should be at an angle of 45° upwards and towards the back of the beck, influencing by its currents the piece only as it is leaving the liquor.

By an intelligent observance of these and other precautions, the continuous system can be advantageously applied to most styles of work, for the temperature, time, and strength of soap are as com-

Fig. 24.



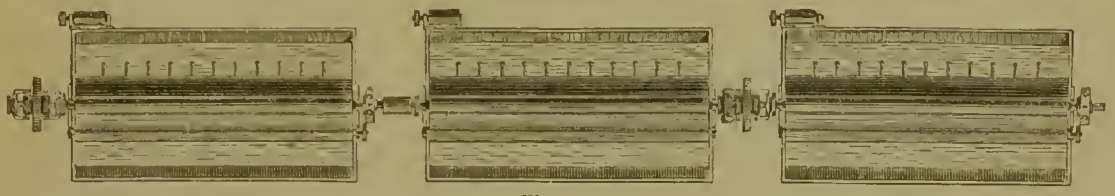


Fig. 25.

pletely under control as in the old interrupted system, and there is a notable saving of labour and damage to cloth. The last beck of the series is kept supplied with hot water and soap, so as to maintain it clean, while the first beck, which wants a good deal of attention, must be so kept supplied with extra soap when required that there is always some lather on the top. The pieces fresh from the washing destroy a good deal of soap, and if the first beck is allowed to break it may dirty the pieces and cause some trouble afterwards; the exhausted and dirty soap liquor is allowed to run freely away from the first beck.

Figs. 24 and 25 show the elevation and plan of a range of three soaping becks working upon the continuous spiral system.

Further remarks upon soaping are general, and do not refer to any special method or apparatus; and when second or third soaping is mentioned, the single beck, or old system, which is still the most largely followed, is that which is meant.

The madder pink style requires the greatest amount of soaping and the most care, and will be first considered. The preliminary soaping for pinks is done at a temperature which should not pass 140° Fahr., and which should be continued long enough to cleanse the cloth and colour from all the impurities not removed by the washing machine. If a much higher temperature be employed in the preliminary soaping, it will be found that the reducing or cutting of the pinks afterwards is less perfect and satisfactory; and if the temperature be much lower, or the time or quantity of soap allowed not sufficient, there will be an unnecessary loss of colour and a probable injury to the whites in the subsequent processes.

The next treatment of pinks is peculiar to this style. It consists in passing them through an acid solution until the colour changes from the crimson shade into a scarlet or orange-toned red. This operation, which is called "avivage" in French, has no fixed name in English, but is widely known as

"cutting." Various acids and acid bodies have been employed, as sulphuric and nitric acids, but the preference is given to a strongly acid solution of tin called the oxymuriate of tin. This preparation is found in trade, but frequently made on the print works by taking say 16 lbs. of the crystals of tin, melting them in their water of crystallization, and adding by small portions 20 lbs. of ordinary nitric acid. There is a violent effervescence and evolution of red fumes, and the oxymuriate is left as a dense somewhat opaque fluid. The quantity of this solution necessary to be employed varies with the quality of water and the depth of colour dyed. The temperature and time also have to be left entirely to the discretion of the dyer. Sometimes the cutting can be done with cold water (that is when the pinks have been dyed at a low temperature and soaped also very lightly); at other times a high temperature must be used. The dyer is guided by the change of colour which takes place, and arrests the operation when it is sufficiently advanced. For the finest and most delicate pinks the change of colour is pushed on until the hue is decidedly orange, but it is mostly preferred to do this at twice, with a soaping between; for fuller and redder pinks the dyer stops the cutting when the colour has only undergone a slight change towards the orange shade. The pieces are washed out of the acid liquid, and then submitted to solution of soap at or near the boiling point. A great deal of colour is dissolved off by the soap, and the boiling with soap is protracted for an hour or more, or repeated with a fresh bath. The beauty of fine reds and pinks depends greatly upon the soaping, and it is sometimes repeated again and again as long as the shade continues to improve. When the pieces have been freed from all loose colour they are frequently boiled with soap in a close pan to give the best possible improvement to the shade. For this purpose a good quality of soap is absolutely necessary; and when the shade of pink is desired to be very bright and fiery, a certain amount of tin crystals is dissolved in the soap. This "panning" is sometimes done under a pressure of 5 lbs. of steam, and is protracted for five or six hours.

This introduction of an acid tin salt in the madder styles may be traced back to the turkey red dyers, but its adoption for printed pink goods is due to the Alsatian printers. It dates from the early years of this century, and gave them a distinct advantage in these colours, which were for long known under the name of Swiss pinks. The French printers may be said as a rule to prescribe or recommend the addition of a certain amount of tin salt to soaping for all styles of work; and their belief is that some tin soap is formed, which becomes part of the colour. Whether this be the real result of such addition, or whether the action be to form a neutral or acid soap, which more easily parts with its fatty matter, or whether it is merely a corrective for a too alkaline soap, is difficult to say. This much may be said from personal experience, that while a really well made soap is so influenced by addition of tin as to exercise a more active impression upon reds in brightening and yellowing them, its cleansing powers are much diminished; and to obtain a good result, an increased quantity must be employed. In fact, a lengthened and varied practice has not convinced the writer that there is any real advantage in using tin crystals along with soap for any kind of madder work where a good quality of soap is employed.

As before stated, the liberal use of soap seems to be a necessity for all good reds from madder and its derivatives and from artificial alizarin. Good dark reds can be dyed from garancin and garanceux, but they do not stand the cutting process; and to obtain them of a lustre and depth approaching madder red, they require an extraordinary amount of soaping—five or six soapings of an hour each not being too much.

*Artificial Alizarin* yields a good heavy red by dyeing. It does not seem to be improved by cutting, and requires a good soaping to yield a fair colour. The process of dyeing with artificial alizarin is carried out the same as for madder; the same mordants somewhat reduced are employed, and the subsequent treatments are the same.

The employment of artificial alizarin or extract of madder in dyeing possesses several advantages over ground madder, which arise from the pure and concentrated state of the colouring matter. The dyeing can be accomplished in a shorter time. If the dyer perceives that the goods are likely to be underdyed from an insufficient amount of colouring matter being used, it is possible to remedy the defect by adding a fresh supply of alizarin or the extract. This could not be done with madder without danger of irregularity, and the only safe remedy was to repeat the dyeing. A less amount of water can be used in dyeing; the washing is more easily effected; baths not quite exhausted can be used for a fresh dye by strengthening up; the soap liquors are cleaner, and throughout it is found that there is much less labour and much less fuel required. It appears that the colours are not quite as fast from artificial alizarin as from madder, and it is found desirable or necessary to steam them between dyeing and soaping. This necessitates drying, and some dyers believe that the goods should be padded in the soap and rosin solution used for pinks, while others believe that simply steaming is sufficient. If this additional operation is found indispensable, there will be styles, such as white ground purples, and other light prints not requiring much dyestuff, which it may be found economical to dye with madder, in order to avoid the delay and expense of the intermediate steaming.

As the topical applications of artificial alizarin and extract of madder yield the same styles as madder, and require the same after treatments, it is proper to treat of them here. The recipes for alizarin colours differ considerably in detail. Some selections are here given of English and German origin, and variations and modifications are afterwards noticed:—

The thickening paste is prepared in advance from—
1 gal. of water.
3 " acetic acid, at 8° Tw.
8 lbs. wheaten starch.
Boiled together, and allowed to go cold.

*Dark Red Alizarin.*

2 gals. of thickening.
1¼ " of alizarin, at 10 per cent.
2 pints acetate of alumina as below.
3 oz. olive or Gallipoli oil.

*Light Red Alizarin.*

6 quarts Senegal gum water.
2 " acetic acid.
2 " alizarin, at 10 per cent.
1 pint acetate of alumina.

*Dark Purple Alizarin.*

2 gallons of thickening.
3 quarts of alizarin.
3 pints of acetic acid.
1 pint of iron liquor at 21° Tw.

*Light Purple Alizarin.*

8½ quarts gum water.
3 " acetic acid.
2 " alizarin.
½ pint acetate of iron at 21° Tw.
1½ " acetic acid.

*Acetate of Alumina for Alizarin.*

1 gallon boiling water.
6 lbs. white acetate of lead.
6 lbs. alum.

The above colours are of English adaptation, and intended for Perkins' alizarin; they present the simplest form of composition for these colours, and are more suitable for working with pigments in five or six coloured patterns than the more difficult style of covered pinks. They are directed to be steamed for two hours, the first hour and half with moist and low steam, and the last half hour with high and dry steam. The following recipes are slight modifications of some furnished by GESSERT BROTHERS of Elberfeld, and are all to be made with an alizarin paste containing 15 per cent. of dry matter:—

*Single Red Grounds Alizarin.*

4 lbs. alizarin, 15 per cent.
5 lbs. acetic acid, 10 Tw.
1 gallon water.
1 lb. olive or Gallipoli oil.
1 lb. acetate of lime at 17° Tw.
2½ lbs. wheaten starch.

These ingredients are well boiled, cooled, and then is added—

1 lb. acetate of alumina at 24° Tw.

*Dark Red Alizarin.*

3¼ lbs. alizarin, 15 per cent.
1 gallon of thickening.
7 oz. nitrate of alumina, 24° Tw.
10 oz. acetate of alumina, 20 Tw.
8 oz. acetate of lime, 24° Tw.

*Red for Pigment Style Alizarin.*

2½ lbs. alizarin, 15 per cent.
1 gallon of thickening.
5 oz. nitrate of alumina, 24° Tw.
10 oz. acetate of alumina, 20° Tw.
7 oz. acetate of lime, 24° Tw.

The thickening for reds is as follows:—

*Thickening for Red Alizarin.*

6 lbs. wheaten starch.
2 gallons water.
4 lbs. acetic acid, 10° Tw.
1 gallon tragacanth gum water.
1½ lbs. olive or Gallipoli oil.

well boiled together.

For dark red, covered with pink, the colour is composed as follows:—

1 gallon of thickening.
2 lbs. of alizarin, 15 per cent.
10 oz. acetate of alumina, 18° Tw.
5 oz. acetate of lime, 24° Tw.

The pink for covering is made by reducing the red with the above thickening, according to the depth of colour required, or the strength and closeness of the engraving.

The acetate of alumina to be used for these colours is not prepared by double decomposition of alum and acetate of lead, but by dissolving precipitated alumina in glacial acetic acid. This is a troublesome process, and, according to the writer's experience, not at all necessary for obtaining good colours. The process is as follows:—The alum is dissolved in a tub of hot water, and crystallized carbonate of soda added as long as any precipitate is produced. The precipitate is washed six or eight times by the decantation method—well understood in colour shops—drained on a calico filter, and then pressed, to obtain it as dry as possible, when it should contain 15 per cent. of dry matter. This pressed paste is then dissolved at a temperature of 80° Fahr. in the strongest acetic acid. On the Continent the glacial acetic acid is used by all the most successful works for topical alizarin colours. This acetate of alumina is a very unstable mordant, and in a short time will deposit nearly the whole of the alumina in its insoluble modification, rendering the mordant useless. It is better to use purified sulphate of alumina, quite free from iron and acetate of lead, in the manner used for making ordinary red mordants.

The nitrate of alumina is made from one gallon of water, 5 lbs. of alum, and 5 lbs. nitrate of lead.

The making and printing of alizarin colours requires the greatest care and cleanliness, because the purity of the shades is injured by the least contamination with metals or other colours. The reds are seen to be very strongly acid, and the thickening cannot be safely boiled in copper pans, unless these have been previously cleaned with the most scrupulous exactness. It is recommended to use enamelled copper or iron pans, or to boil the thickening in an earthenware vessel. In working, a wooden colour-box is to be employed, and, if possible, a composition or silver-nickel doctor, instead of a steel one. If only a steel doctor will clean the roller, it may be covered with engravers' varnish on the side next the colour, up to within a quarter of an inch of the edge, and the mandrill must be lapped near the roller, so that the colour will not come in contact with it. If, during the working of a pink cover, the machine be stopped for twenty seconds, the doctor shows a dark mark all across the piece, and for a yard or more the shade is perceptibly injured by the action of the iron dissolved from the doctor.

The pieces may be steamed immediately after printing. If covered pinks are being worked the dark pink never comes up with satisfactory distinctness unless it is steamed separately, that is, before

covering: a half-hour's steam is sufficient. For the dark pink the time of steaming is usually two hours; and though many different ways of steaming have been proposed, it seems proved that no method is better than having an abundance of low and quite damp steam. In endeavouring to get the steam low and moist from a high pressure supply, care must be taken that there is sufficient of it to make certain that the cloth is speedily heated up to 212° Fahr., and kept at that temperature during the whole time: any higher temperature is not only unnecessary, but very likely to yield dull flat colours, which cannot be brightened by soaping.

After steaming, the goods may be hung in the ageing room for twenty-four hours, or they may pass on directly to the dye house. There are different methods of commencing the treatment in the dye house. In some cases the goods are passed in the dunging dolly through warm water and chalk. Silicate of soda is also employed; and for purples, arseniate of soda is sometimes used, and frequently nothing but water is used. The pieces are only from one to two minutes in the dunging dolly, and it may be looked upon as only a convenient method of wetting out preparatory to washing. The washing must be continued until the loose matters are removed; for if the pieces go imperfectly cleaned into the soap, the liquid becomes very dirty, and the whites and colours are injuriously affected.

The soaping is commenced at about 140° Fahr., and there must of coarse be sufficient soap to give a free lather. Here, as in other cases referred to previously, the Continental colourists insist upon the benefits to be derived from the addition of tin crystals to the soaping liquor; and here, as before, the writer never could satisfy himself that there was any advantage in it, while it certainly destroys soap. During the first soaping the dyer can form a tolerably correct idea as to whether the colour will turn out good or not. If the red and pink seem hard, that is, resist the action of the soap, and if the soap liquor only acquires a brownish and not a full red colour, an inferior result may be predicated. Either the colour has not been well made, and the proportion of mordant has been too great for the alizarin, or the printing has not been successful, not full enough, and probably accompanied by sticking in and a separation of the colouring principle from the mordant, or the steaming has been too high, or something else wrong has occurred. If the soap liquor becomes fairly, even deeply coloured, and the colours themselves seem softening and yielding to the action of the soap, a good result may be anticipated. The temperature must not be pushed much beyond 140° Fahr. for half an hour; for in well charged patterns much colour is removed, and the soap liquor becomes very dirty. The soaping is repeated at least twice more for reds and pinks, and at a higher temperature (say up to 180° Fahr.); and if it seems desirable the goods are boiled in clean soap for an hour or longer.

It will thus be seen that the artificial alizarin applied topically requires as much soaping, and probably longer soaping, than the same styles from madder, in order to obtain a colour similar to that from madder. Setting aside those designs in which pink, red, and purple from alizarin are combined with black, blue, green, and orange from aniline or pigments, and in which there is no question of comparison between madder and alizarin, it may be asked what are the advantages derived from the employment of alizarin in the old madder styles. The advantages are—first, in the cost, which may, however, be only a temporary advantage; and secondly, in the facility of application, owing to which establishments that were never able to do the highest class of madder work, either in pinks or purples, can produce a very close imitation of them, and supply the wants of the market. In other respects it may be said that though artificial alizarin gives results very similar to madder, the best alizarin colours are not equal in solidity or beauty to the best madder colours; and apart from the cost of the primary material, the expenses of application are rather in favour of madder, the alizarin colours requiring more steam and more soap than madder colours.

With regard to the composition of alizarin colours the following notes may be recorded:—Nitrate of alumina tends to give a yellower red than the acetate. The nitrate cannot of course be used without acetate of alumina or acetate of lime in conjunction, on account of its destructive action upon the cloth. The use of acetate of lime is believed to improve the regularity and the fastness of the colour. Tragacanth gum water, which is not much used in this country, is of very extended use on the Continent for many colours, and is thought to contribute to their easy working in the printing machine. The large amount of oil employed in the alizarin colours is with the intention of improving the working, and causing at the same time a fixing of it upon the cloth to assist as a mordant. The oil should be of good quality. It is sometimes recommended to use the emulsive oil, as employed in turkey red, but it possesses no superiority over the ordinary oil.

Alizarin gives a pleasant shade of chocolate with chromium mordant by steaming; but it is rarely employed, requiring as much colouring matter as strong red to obtain full shades.

The soaping of madder purples requires no particular notice. They require a good quality of soap; and though not absolutely requiring the presence of fatty matters, they are much improved by them, and the colours apparently raised as if in relief upon the surface of the cloth. This effect can only be obtained by the free use of a well made soap. The temperature for ordinary bold purples should not exceed 180° Fahr. For a softer and more delicate shade of purple the goods may be "panned" or boiled with soap in a close vessel for one or two hours, and in this case the addition of crystals of tin has a decided influence in reducing the tone of the colour.

Garancin and pincoffin, or commercial alizarin dyed goods, are sometimes slightly soaped to improve

the colours; garancin reds are improved by steaming after dyeing. Madder pinks are also often steamed after dyeing and before soaping; this hardens the colour, and is useful in cases where the light pink is not well up. For general work it is not to be recommended, because it injures the shade.

Flowers of madder behave in every respect like madder, but do not stain the whites so much, and do not require so much soaping to bring up the colours.

Clearing of Whites.—Formerly the dye house operations concluded by passing the goods in a warm and very dilute solution of bleaching powder, to remove the tinge of colour on the whites. This operation is now seldom performed in the dye house, and the clearing may be said to be universally accomplished by the padding machine and steam box, which should be in connection with a drying machine. After the final washing in the dye house the goods are therefore passed through the squeezers, to remove as much water as can be expressed by mechanical means, or in the non-continuous process they are partially dried by the hydro-extractor; and those goods which do not require much clearing are at once sent on to the drying machine, or in the still wet state they are chlored and dried. But generally the chloring in the wet state is confined to garancin styles which have strong colours, and the whites of which require strong treatment to clear them, and they are chlored again a second time in the dry state.

The chloring machine consists essentially of a box to contain the solution of chloride of lime,

Fig. 26.

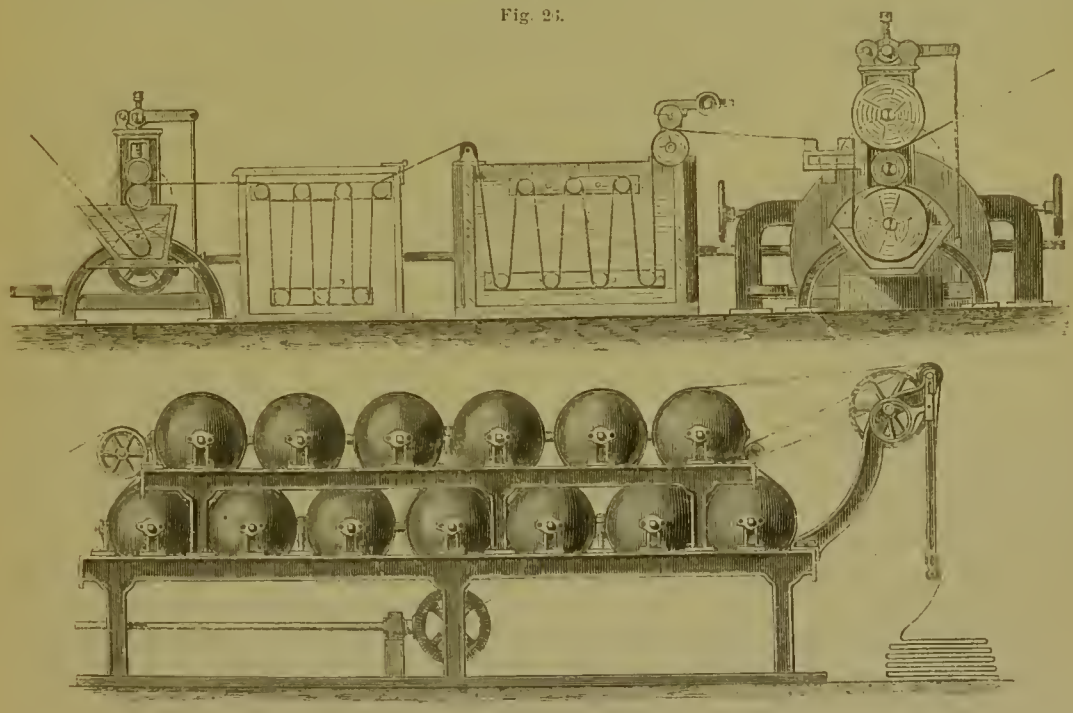


Fig. 27.

and two rollers working in a frame and placed immediately over this box; the upper roller is covered with thick india-rubber, and the lower may be of brass or copper. The cloth either passes directly between the rollers, receiving the bleaching liquor from the under roller, which, revolving in the fluid, carries up a sufficient portion, or, what is much preferable on the ground of regularity and certainty, the box is provided with a roller or fixed rail near the bottom, and the piece passes under this and consequently right into the bleaching liquor, and then between the metal and india-rubber covered roller, to express the excess out. Attention must be directed to the state of the india-rubber roller, which must be kept in good order, or else there will be an unequal amount of the bleaching liquor on different parts of the cloth, with the probable result of the middle or sides of the piece being either under or over cleared. The cloth passes directly into the steaming box, which is placed as near as possible to the frame and rollers. This box is provided with small copper rollers in the interior, by means of which the piece travels three or four times backwards and forwards; and steam is admitted by perforated pipes so arranged that it blows directly upon the whole width of the piece; and the steam must be in such quantity as to raise the temperature of the piece almost instantly to the boiling point, and be in such excess that it blows out freely and forcibly at the slits which serve for the entering and exit of the cloth.

Fig. 26 shows a chloring arrangement combined with a starching mangle; and Fig. 27 shows the drying machine which is connected, and over which the starched goods pass to be dried.

The strength of the solution of bleaching powder must evidently vary with the nature of the goods under treatment; for heavy garancin styles it may be as strong as 1° Tw., or stronger, while for delicat · shades of purple, and for some of the aniline colours, it must not be one-fiftieth of that strength. Some difference will arise from the quantity of liquor which the piece is allowed to carry with it, depending upon the set of the rollers, but as a rule the piece should have a good nip, and it is preferable to have a smaller quantity of a strong liquor than a large quantity of weak liquor.

In the best arrangements of machinery the cloth is passed on without stopping into the water mangle, where it passes through a trough of water to wash out the remains of the bleaching liquor; then between wooden bowls and a brass roller to straighten and squeeze it; and lastly, on to the tins of the drying machine.

Finishing Operations.—With the exception of turkey red, and sometimes heavy blue styles, all prints are, as a rule, submitted to a finishing operation, the object of which is to stiffen, smooth, and press them for the market. This final process does not involve any chemical principles, and might seem so subsidiary to an outsider as not to call for any detailed notice; but it is a matter of the first importance in the trade, and at times a subject of much trouble and anxiety. When the artist, the chemist, and the machinist have together succeeded in producing an elegant print, good in design, perfect in execution, and rich and fast in colour, they might think their work done; but unless the finish be satisfactory, they will find all their labour and skill have been thrown away on unsaleable goods. The fastidiousness and capriciousness of buyers from different markets, the importance they attach to the degree of stiffness, the amount of gloss and the peculiarity of feel of a finished print, the difficulty of conveying their meaning in words, and the apparently contradictory and incompatible qualities they demand, are a frequent perplexity to the print works manager, and he has to call to his aid experience, machinery, and complex processes to satisfy the wants of the market. Nearly every market has its own favourite finish, but we can only give general ideas and hints as to how various kinds of finish are produced, so as to communicate the desired stiffness, gloss, and feel, without injuring the colours.

As above stated, some styles are sent to market unstiffened, but this is exceptional. In the case of turkey reds the lustre and fine softness of the colour is so much injured by starching, that in most markets they are sold either entirely without stiffening, or with very slight stiffening, and the only finishing operation they are subjected to is a slight calendering or mangling, to lay the cloth smooth and free from creases. The employment of the water mangle, and the squeezing of the pieces full width, contribute greatly to giving an even and uniform surface to calico. Navy blues, for similar reasons, are completed with a soft finish, and to heighten the depth of colour are sent as damp as possible to the market. Other prints are rarely made up without some stiffening, but are sometimes required by certain markets. To the genuine connoisseur and critic the colours on a print never look so well as when unstiffened.

The home market in Great Britain takes ordinary good prints with a medium amount of stiffening, and does not require any glaze or lustre on the surface. The old starching apparatus, and one still much in use, consisted of a framework holding three rollers, the full width of the calico to be finished, the centre roller of small diameter of copper or brass, and the two large rollers of hard wood, usually sycamore or maple. The starch boiled up in a pan, and mixed with blue, is contained in a trough; the calico to be finished is drawn through the starch, and the excess pressed out by causing the cloth to pass between the wooden and metallic rollers. Sometimes only one wood and one metal roller are used; and in other cases the cloth is not drawn through the starch, but removes a sufficient quantity of it from the large wooden roller which revolves in it. After receiving the starch, the calico passes over the drying machine, and then is passed between wooden and metal rollers to smoothen or mangle it, as much pressure being put on as the apparatus will bear. The remaining operations are measuring, folding, and making up.

In this somewhat old-fashioned method, the points to be attended to are the thickness of starch, the quality of the starch, and the quantity put on the cloth. The thickness of the starch varies according to the amount of stiffness required, and the quality of the calico; for superior kinds of calico it is used thin, for low qualities it is used thicker, in order to give it more weight and a substantial appearance. The kind of starch to be employed depends in a great measure upon the kind of finish required. Perhaps the general demand in the trade is for a finish which gives the appearance of fulness, without feeling stiff; what is called the "clothy" feel. Sago flower and potato starch are good bases to go upon, and there are several mixtures of starches sold in the trade under the name of "finishing starches," which are of various composition, being mixtures of sago starch, potato starch, maize flour, rice starch, and other similar products, which are found more or less suitable for the purposes of printers. In the boiling of the starch, it will generally be found that the lower the temperature at which the starch can be dissolved, the better it is for finishing: if the starch be over boiled, it acquires a gummy character, and the calico is found to have a thin, hard, and flinty finish, with a tendency to curl up when left in a dry place. To counteract the stiffness and harshness which inferior starch or too much starch communicates to the cloth, it is customary to mix some fatty matter, or glycerine, or soap, with the boiled starch; tallow, stearine, bone fat, or the so-called finishing pastes, which are usually nothing but very watery soaps, can be employed for this purpose. In finishing prints containing delicate shades, care must be taken that the soap or printing pastes are not too alkaline in their nature,

for many fine shades are dulled by a trace of free alkali. Glycerine is useful as giving a softer feel to the finish, and preserving it somewhat humid; some finishes where great weight is required in the cloth have been made entirely of colourless soluble gum, with a large proportion of glycerine. In order to improve the whites, and in some cases even to give a distinct blue tinge to the whites, ultramarine blue is mixed with the starch; other kinds of blue, such as Prussian blue or aniline blue, may be used, but preference is given to a very fine, specifically light variety of ultramarine. It may be noted, that though bluing gives a brighter appearance to the finished print, it is a mistake to suppose that an extra quantity of blue in the starch will neutralize or overpower bad whites; it is only a good white which shows up the agreeable azure tinge of the blue used in finishing.

The inconveniences of the old method of stiffening prints was first felt when dark garancin style came into vogue some twenty years ago. The colours, after finishing, looked dull and flat compared with the unstarched print, and this was soon found to be a defect inherent to the system of applying the starch in stiffening. The layer of starch, which covered the face as well as the back of the piece, not only obscured the colours by its partial opacity, but destroyed the bloom by pasting together, so to speak, the velvety surface of the cloth. To obtain the necessary stiffness of the calico without covering the colours, it was evident that the starch should be applied only upon the back of the tissue, and this could be accomplished by various means, the most convenient of which at first was by padding in the printing machine with an engraved roller. This was followed by the introduction of the back-starching machine, patented by JONES, of Rhodes Printworks. The means used in this machine were chiefly an engraved copper roller revolving in a trough of starch, the excess of starch removed by a doctor, and the cloth drawn with a slight pressure over the engraved roller, which revolved rapidly in a direction opposite to the motion of the cloth. By this contrivance an uniform layer of starch was spread over the back of the piece, and as but little direct pressure was acting upon it, only a small portion was forced through to the face to interfere with the colours of the dye. The drying of the cloth, thus smeared with a superficial layer of starch, presented some difficulties; it could not be run upon the drying tins like cloth uniformly impregnated with starch, for when the starched side touched the heated metal the starch formed a thin semi-solid sheet, for which the metal had more attraction than the calico, and it either adhered to the surface of the drying tins, or came off in semi-transparent films and flakes, but a small portion remaining on the cloth. To avoid this a series of about four skeleton drums, called "lagged rollers," were arranged above the drying tins, and the face of the cloth only came into contact with the steam-heated cylinders, and by passing over four or five of these the starch was sufficiently consolidated to permit the piece to be dried by the usual back and front passage on the remaining tins of the drying machine. To insure a proper adhesion of the starch by means of a sufficiently rapid drying, it is recommended that the drying machine be worked at a pressure of say 15 lbs. of steam in the tins.

Figs. 28 and 29 show the elevation and plan of the back-starching arrangement as constructed by GADD of Manchester.

It is evident that by this process of applying starch it would be possible to mix with it perfectly opaque materials, such as china clay or barytes, and this is frequently done with low qualities of cloth to give them the weight and feel of a better article.

In the bleaching and dyeing operations calico is elongated to a certain extent, and becomes narrower in proportion; in order to restore a portion of the width lost it is now usual to subject it to the action of certain apparatus, which are known as widening or breadthening machines. There are several different arrangements for this purpose, but the tendency is to employ a modification of one long in use by the white finishers, which consists of two rollers with circular grooves revolving one over the other, the raised parts of one roller fitting into the depression grooves of the other. The cloth is passed between the two rollers, and the edges or selvedges being held by a rope running in a groove, the effect of the action of grooved rollers is to press the already tightened piece into the depressions, and so stretch it in the direction of its width. This operation is usually performed after the starching, and before the mangling or calendering. STARK of Thornliebank has recently patented an arrangement in which these grooved rollers are combined with the drying machine, and the widened cloth immediately passes from the grooved rollers on to the drying tins, and the breadthening effect is made more permanent. DENNISON'S machine, also much used, consists of two large pullies set upon an axis in such a way that instead of being vertical and parallel they are oblique, and incline to one another for one-half the diameter, and diverge from one another for the other half, so that revolving on one shaft the edges of the pullies are, in one position, nearer to each other than in the opposite position. The cloth to be widened is fed on to the pullies at the point where they are nearest, and the selvedges being held by a strong travelling band of gutta-percha the cloth is forcibly stretched, and its width may be safely increased about one-fifteenth.

For some special classes of prints there are special finishing apparatus. It is only necessary to refer to the "stentering" finish used for muslins and fine cambrics, sometimes also for ordinary cloth bearing check patterns or cross stripes. The stentering frame is commonly a long framework upon which travel endless bands bearing fine pin points. The selvedges of the cloth to be finished are held by these pins; a to and fro motion of the endless bands serves to strengthen the position of the weft-threads of the fabric, and provision is made for applying the starch or size for stiffening, and also for drying the tissue, while it is still held distended by the pins and travelling onwards.

It has been stated that the usual finish for the home market in Great Britain is given by as forcible a pressure as can be obtained from wooden bowls acting upon a brass roller, and between which the cloth is passed; but several foreign markets require a higher finish, that is, a gloss or glaze upon the surface of the print. To communicate this finish

Fig. 28.

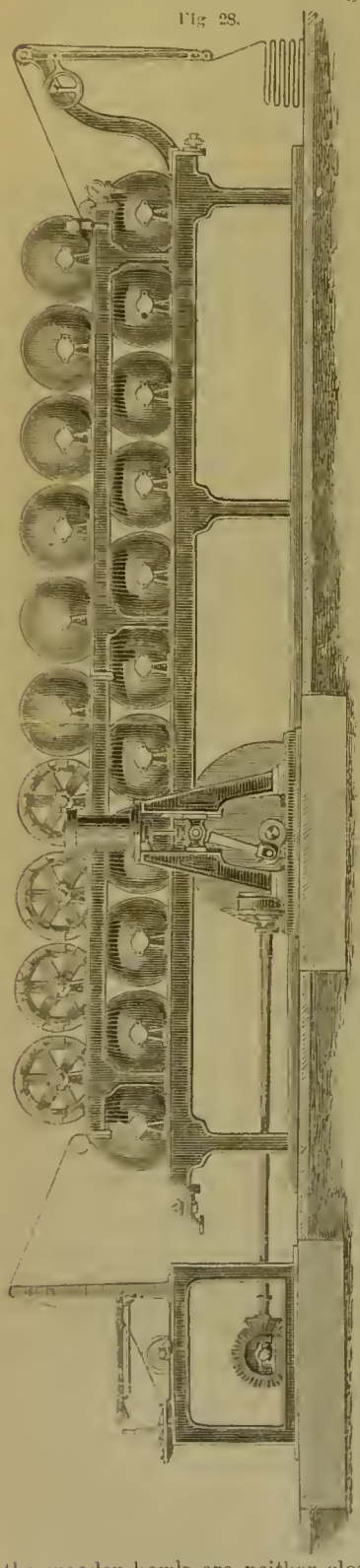
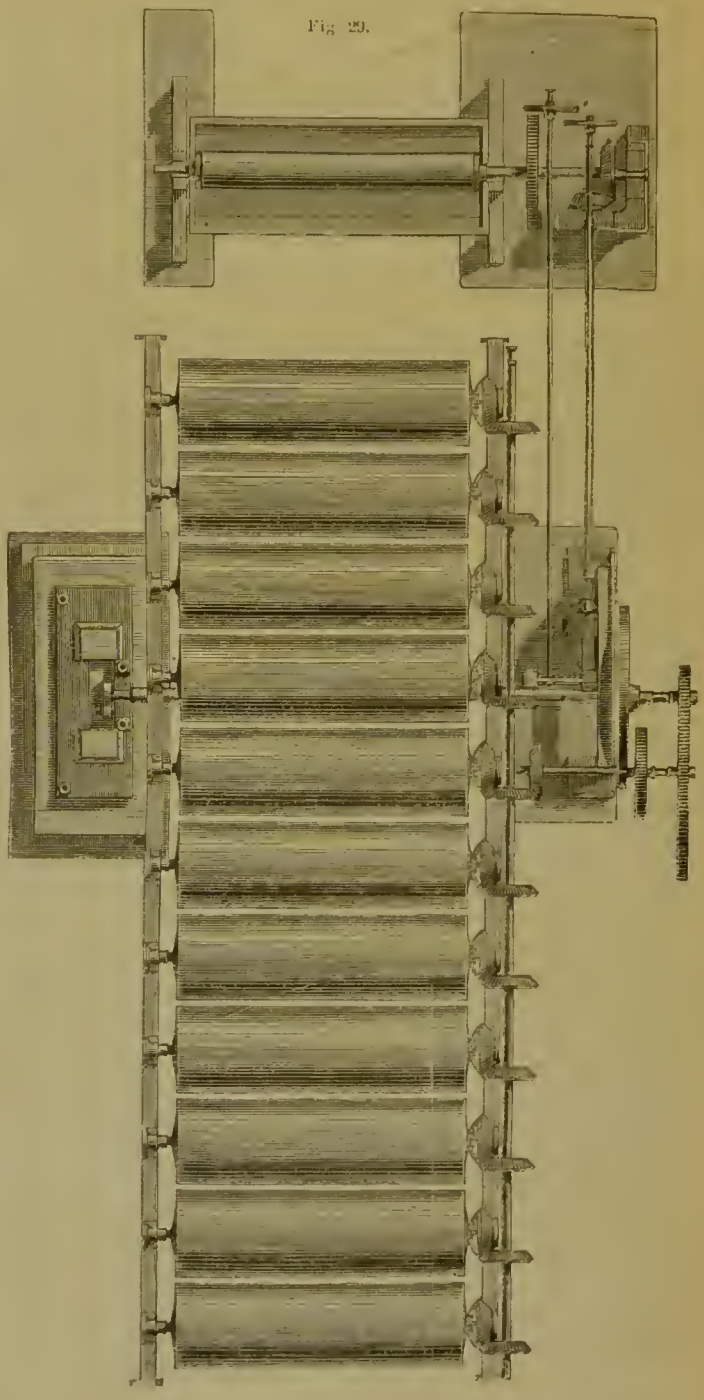


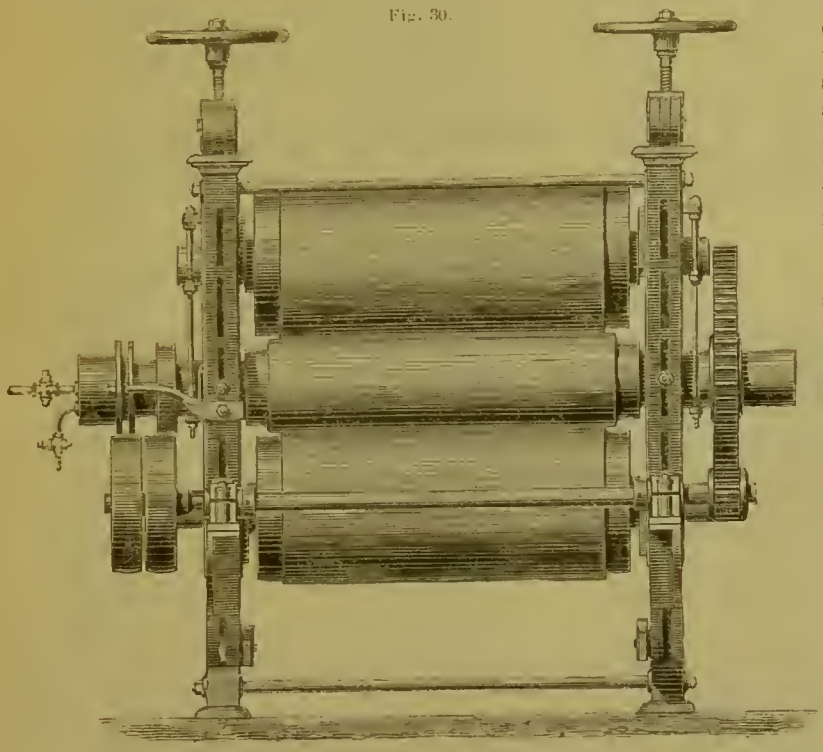
Fig. 29.



the wooden bowls are neither close enough in texture nor strong enough in material to resist the enormous pressure required; and bowls are made by compressing paper or cotton upon iron centres by hydraulic rams, until these usually soft or fragile substances acquire a density and hardness almost inconceivable. When these paper or cotton bowls are mounted on a suitable framework, along with

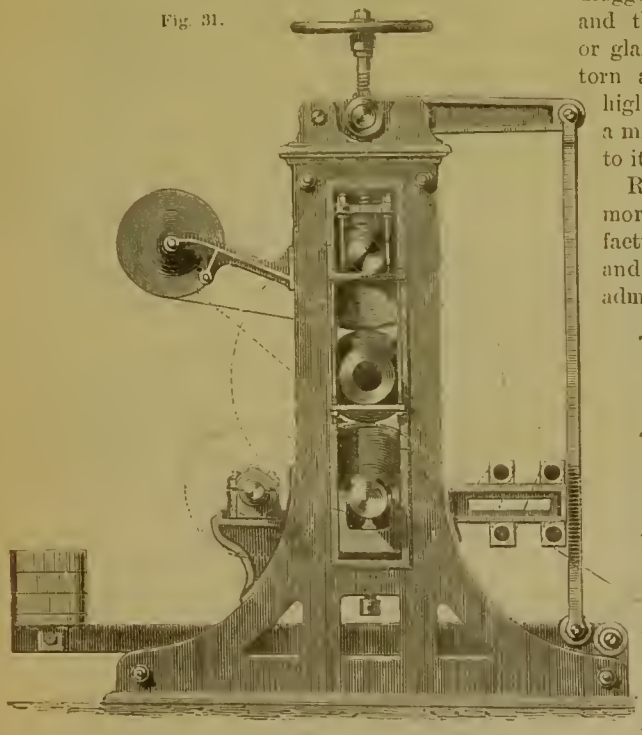
rollers of the hardest iron, the machine is called a calender.

Fig. 30.



The Swissing calender, as seen in Figs. 30 and 31, consists of two paper bowls, with an intermediate iron bowl, and the weight is applied by means of screws and levers; in most cases it is necessary to heat the iron bowl, which is for that purpose made hollow, and heated either by steam or by placing in it heated irons of a suitable shape. When the starched and damped goods are passed through this calender, the surface next to the metal acquires a gloss or polish by the flattening down of the threads, and the heavy pressure brought to bear upon it.

Fig. 31.



When the highest degree of gloss is required, as for some kinds of furniture prints, it is necessary to have recourse to the friction calender. The friction calender has the metallic bowl usually placed on the top of the two paper bowls, and is driven by a separate wheel. The driving wheels are so speeded that the iron bowl moves faster than the paper bowl, and being pressed with an enormous weight upon it there is a frictional or rubbing effect in addition to the dead pressure. The iron bowl may travel, say 40 inches, while the paper bowl immediately in contact with it travels only 39 inches; the iron bowl is therefore dragged over the cloth which is between them, and thus communicates a high degree of lustre or glaze to the cloth. To prevent the cloth being torn asunder by this dragging, the iron bowl is highly polished, and usually kept lubricated with a minute portion of wax or similar matter, applied to its surface by a properly arranged pad.

RECEIPTS—*Mordants.*—In the preparation of the mordants we distinguish two stages: the manufacture of the red liquor, or acetate of alumina, and its subsequent adaptation for printing by admixture with thickeners.

*Standard Red Liquor—*

| | | |
|---|---|---|
| Alum, | 40 | lbs. |
| White sugar of lead, | 25 | " |
| Boiling water, | 10 | gals. |

*Strong Red Liquor—*

| | | |
|---|---|---|
| Alum, | 11 | kilos. |
| White sugar of lead, | 82·5 | " |
| Boiling water, | 32 | litres. |

*Five fourths Red Liquor—*

| | | |
|---|---|---|
| Alum, | 625 | grams. |
| Sugar of lead, | 450 | " |
| Boiling water, | 2 | litres. |

*Resist Red Liquor—*

| | | |
|---|---|---|
| Acetate of lime at 24° Tw., | 90 | gals. |
| Sulphate of alumina, | 272 | lbs. |
| Ground chalk, | 34 | " |

*Another Resist Red Liquor—*

| | | |
|---|---|---|
| Water, | 1 | gal. |
| Alum, | 5 | lbs. |
| Sugar of lead, | 2½ | " |
| Soda crystals, | ¼ | " |

The subjoined formulæ have a great reputation for madder-work in France:—

| | A | B. | C. |
|---|---|---|---|
| Alum, | 16 kilos. | 8·0 kilos. | 10 kilos. |
| Sugar of lead, | 12 " | 8·5 " | 10 " |
| Boiling water, | 62 " | 6 0 " | 20 " |

*Red Liquor for Garancin Work* (to stand at 15° Tw.)—

| | |
|---|---|
| Alum, | 25 kilos. |
| Sugar of lead, | 19 " |
| Water, | 80 litres. |

*Strong, ditto*—

| | |
|---|---|
| Alum, | 25 kilos. |
| Sugar of lead, | 20 " |
| Water, | 63 litres. |

All red liquors should be prepared from the purest materials, the presence of iron in the alum being especially to be avoided. None of them should be made in very great quantity, as they are apt to undergo changes in their composition on long standing. This relates especially to the stronger kinds.

The following are a selection of mordants, or as they are technically called colours, as thickened and made ready for use:—

| | Dark Red. | Medium. | Light. |
|---|---|---|---|
| Red liquor at 13° Tw., | 1 litre. | 1 litre. | 1 litre. |
| Water, | 1 " | 4 " | 15 " |
| Starch, | 240 grms. | 0 grms. | 0 grms. |
| Calcined starch, | 60 " | 2 kilos. | 6 kilos. |
| Gallipoli oil, | 30 " | | |
| Peach liquor, | 164 " | | |

*Another Red*—

| | |
|---|---|
| Garancin red liquor at 15° Tw. (see above), | 1 litre. |
| White starch, | 110 grms. |
| British gum, | 75 " |

*Bright Red*—

| | |
|---|---|
| Strong red liquor (see above), | 1 litre. |
| Acetic acid at 1½° Tw., | 4 litres. |
| British gum-water, 750 grms. per litre, | 9 " |
| Pipe clay water, 1 kilo. per litre, | 5 " |

*Deep Red* (for fine patterns)—

| | |
|---|---|
| Red liquor at 9° B., | 1·0 litre. |
| Water, | 6·0 " |
| Brazil wood liquor, | 10·0 litres. |
| Acetic acid at 1½ Tw., | 5·0 " |
| Alum, | 2½ kilos. |
| Crude sugar of lead, | 2½ " |
| White starch, | 3 " |
| Gallipoli oil, | 375 grms. |
| Nitrate of copper at 109½° Tw., | 375 |

*Another Red*—

| | |
|---|---|
| White starch, | 2 kilos. |
| British gum, | 4 " |
| Strong mordant, | 10 litres. |
| Lima wood liquor, | ¼ litre. |
| Gallipoli oil, | ½ " |
| Pyroligneous acid, | 5 litres. |
| Muriatic acid, | ¼ litre. |
| Pyrolignite of lime, | 1 kilo. |
| When cold add— | |
| Tin crystals, | 750 grms. |

*Roses or Pinks*—

| | | |
|---|---|---|
| Boiling water, | 30½ litres. | 38 grms. |
| Acetic acid at 11½° Tw., | 1½ " | 2 " |
| Mordant, 5-4th, | 8 " | 2½ " |
| Dark calcined starch, | 20 kilos. | 20 kilos. |
| Gallipoli oil, | 375 grms. | 375 grms. |
| Oil of turpentine, | 375 " | 375 " |

*Resist red, Dark*—

| | |
|---|---|
| Resist-red liquor at 18° Tw., | 12 gals. |
| Flour, | 24 lbs. |
| Boil well, and when cold add tin crystals, | 12 lbs. |

This is used to resist chocolate "covers."

*Resist-red, Dark*—

| | |
|---|---|
| Resist-red liquor at 18° Tw., | 6 gals. |
| Flour, | 12 lbs. |
| Boil, and add when cool tin crystals, | 3 " |

This serves to resist purple "covers."

| | Purple 8. | Purple 32. |
|---|---|---|
| Boiling water, | 48 litres. | 48 litres. |
| Black liquor at 10 B. | 6 " | 1½ " |
| British gum, | 36 kilos. | 30 kilos. |
| Oil of turpentine, | 375 grms. | 375 grms. |

*Purple Fixing Liquor*—

| | |
|---|---|
| Arsenious acid, | 22½ lbs. |
| Soda crystals, | 25 " |
| Water, | 2 gals. |
| Boil till dissolved. Add to pyroligneous acid heated to 120°, | 50 " |
| Let stand till all tarry matters are settled, and add muriatic acid, | 3 quarts. |

*Black*—

| | |
|---|---|
| Pyrolignite of iron at 10° B., | 32 litres. |
| Calcined starch, | 10 kilos. |
| Water, | 24 litres. |
| Bark liquor at 18° B., | 2 " |
| Logwood liquor at 17° B., | 2 " |
| Olive oil, | ¼ " |

*Browns and Chocolates*—

In preparing these the following red liquors are employed:—

| | |
|---|---|
| Z. Alum, | 10 kilos. |
| Sugar of lead, | 10 " |
| Water, | 20 litres. |
| Y. Alum, | 144 kilos. |
| Sugar of lead, | 144 " |
| Water, | 660 " |
| Soda crystals, | 4 " |

With these are compounded—

| | |
|---|---|
| Mordant Z, | 8 litres. |
| Black liquor at 10° B., | 4 " |
| Bark liquor at 20° B., | ½ " |
| White starch, | 2·5 kilos. |
| British gum, | 250 grms. |
| Gallipoli oil, | 90 " |

Another—

| | | |
|---|---|---|
| Mordant Y, | 12 litres. | 16 litres. |
| Black liquor at 10° B., | 2 " | 4 " |
| Bark liquor at 20° B., | ¾ " | ½ " |
| White starch, | 3 kilos. | 4 kilos. |
| British gum, | 375 grms. | 375 grms. |
| Gallipoli oil, | 125 " | 125 " |

*Brown, for Garancin*—

| | |
|---|---|
| Catechu, | 2 lbs. |
| Water, | 53 ozs. |
| Sal-ammoniac, | 6½ " |
| Boil, strain, and add gum-water, | 106 grms. |
| Nitrate of copper at 80° Tw., | 16½ ozs. |
| Acetate of copper, | ½ pint. |

If a redder tone is needed red liquor may be added.

*Chocolate*—

| | |
|---|---|
| Black liquor at 24° Tw. | 3 gals. |
| Red liquor at 18° Tw. | 9 " |
| Flour, | 24 lbs. |
| Oil, | 1 pint. |

*Chocolate for Garancin—*

| | |
|---|---|
| Red liquor at 18° Tw., | 2 gals. |
| Black liquor at 8° Tw., | 5 quarts. |
| Flour, | 5 lbs. |
| Logwood decoction, to sighten, | ½ pint. |

*Drab—*

| | |
|---|---|
| Brown standard, | 2 gals. |
| Muriate of iron (proto) at 9° Tw., | 2 quarts. |
| Acetate of copper mixture, | 6 " |
| Gum-substitute water (4 lbs. per gal.), | ½ gal. |

If this is to be used for garancin the quantity of gum-substitute water is increased to 2 gallons.

*Brown Standard*, referred to above—

| | |
|---|---|
| Water, | 25 gals. |
| Catechu, | 100 lbs. |
| Boil for about 6 hours, and add acetic acid, | 2¼ gals. |
| Water to make up to 25 gals. Let it stand for two days and run off the clear liquid. Heat it to 130° Fahr., and add sal-ammoniac, | 48 " |

Let stand, after dissolving for two days, run off the clear, and thicken it with 4 lbs. gum Senegal per gallon.

*Acetate of Copper Mixture—*

| | |
|---|---|
| Blue vitriol, | 2 lbs. |
| Sugar of lead, | 2 " |
| Boiling water, | 2 quarts. |

Dissolve, let settle, and let down with water to 18° Tw.

*Stannous Mordants.*—The only preparations of tin used by English calico printers are :—

1. Tin crystals (protochloride of tin).
2. Double muriate at 120° Tw. (protochloride of tin in solution).
3. Bichloride of tin in solution at 120° Tw. (known also as perchloride, permuriate, and oxymuriate).
4. Pink salt (double chloride of ammonium and tin, ammonic perchloride of tin).
5. Stannate of soda.

Of these compounds one only, the stannate of soda (otherwise known as "preparing salts"), is in practical use, the stannates of potash and lime and the stannites being rarely, if ever, employed. On the small scale the stannate of soda is obtained by treating a strong solution of perchloride of tin with concentrated soda lye till the precipitate which falls at first is redissolved. As thus prepared it contains, of course, chloride of sodium as an impurity. Greenwood and Mercer obtain the stannate by putting 22 lbs. of caustic soda, 1 gallon weighing 13½ lbs., into an iron crucible set over a fire, and heated to low redness. When steam is no longer given off, 8 lbs. nitrate of soda and 4 lbs of common salt are added. When the mixture is near the melting point 10 lbs. of feathered tin are added, and stirred in. The mixture grows red-hot and assumes a pasty consistence. When cold it is dissolved in water; allowed to stand, protected from the air till the impurities subside, when the clear liquid is drawn off and evaporated down. In hydrated or crystalline stannate there is present from 20 to 27 per cent. of water. Common salt is sometimes added as an adulterant to a very considerable extent.

Compound preparing salts, such as silico-stannates, arsenio-stannates, phospho-stannates, and alumino-stannates, have been from time recommended on high authority, but they have never come into general use in the trade.

*Spirit or Fancy Colours.*—The following are a few of the colours in use :—

*Black—*

| | |
|---|---|
| Logwood liquor at 8° Tw., | 2 quarts. |
| Water, | 2 " |
| Copperas, | 5 ozs. |
| Starch, | 1½ lbs. |

After boiling stir in nitrate of iron at 79° Tw., 5 ozs. (measure).

*Blue—*

| | |
|---|---|
| Water, | 2 gals. |
| Yellow prussiate, | 2 lbs. |
| Alum, | 12 ozs. |
| Starch, | 2½ lbs. |

After boiling and cooling down to 110° Fahr., add—

| | |
|---|---|
| Nitrate of iron at 82° Tw., | 1½ pint. |
| Oxychloride of tin at 100° Tw., | 3 pints. |

*Chocolate—*

| | |
|---|---|
| Sapan liquor at 9° Tw., | 1½ quart. |
| Bark liquor at 13° Tw., | 1 pint. |
| Logwood liquor at 10° Tw., | 1 quart. |
| Starch, | 1 lb. |

After boiling, cool down to 108° Fahr., and add—

| | |
|---|---|
| Oxymuriate of tin at 100° Tw., | ½ pint. |
| Nitrate of copper at 80° Tw., | ½ " |
| Olive oil, | ½ " |

*Pink—*

| | |
|---|---|
| Sapan liquor at 15° Tw., | 2 quarts. |
| Gum-water, 6 lbs. per gal., | 2 " |
| Sal-ammoniac, | 4 ozs. |
| Bichloride of tin at 120° Tw., | ½ pint. |

*Pink for Blocking Madder Work—*

| | |
|---|---|
| Brazil wood liquor at 9° Tw., | 2½ gals. |
| Sal-ammoniac, | 1½ lb. |
| Pink salt, | 4½ lbs. |
| Sulphate of copper, | 1 lb. |
| Oxalic acid, | 2⅝ ozs. |
| Water (measure), | 18 " |
| Gum Senegal water (6 lbs.), | 2¼ gals. |
| Bichloride of tin, 120° Tw., | 1 pint. |

*Purple—*

| | |
|---|---|
| Logwood liquor at 9° Tw., | 2 quarts. |
| Water, | 2 " |
| Copperas, | 5 ozs. |
| Starch, | 1 lb. |

After boiling, add—

| | |
|---|---|
| Muriate of iron at 80° Tw., | ½ pint. |
| Oxymuriate of tin at 120° Tw., | ½ " |

*Red—*

| | |
|---|---|
| Sapan liquor, | 1½ gal. |
| Verdigris, | ½ lb. |
| Sal-ammoniac, | ½ " |
| Starch, | 2¼ lbs. |

Boil, let cool, and add—

| | |
|---|---|
| Oxalic acid, | 8 ozs. |
| Pink salt, | 2½ lbs. |

*Yellow—*

| | |
|---|---|
| Berry liquor at 10° Tw., | ½ gal. |
| Alum, | 4 ozs. |
| Starch, | 8 " |

After boiling, add—

| | |
|---|---|
| Double muriate of tin, | ½ pint. |

*Colours to be Fixed by Steaming :—*

*Black (Cylinder)—*

| | |
|---|---|
| Logwood liquor at 12° Tw., | 1 gal. |
| Gall liquor at 9° Tw., | 1 quart. |

| | | |
|---|---|---|
| Mordant (as given below), | 1 | quart. |
| Flour, | 2 | lbs. |
| Starch, | 6 | ozs. |

Boil for about ten minutes, and then stir in half a pint of nitrate of iron.

*Mordant* referred to—

| | | |
|---|---|---|
| Acetic acid, | 1 | gal. |
| Acetate of copper at 3° Tw., | 1½ | " |
| Black liquor at 24° Tw., | 1½ | " |
| Red liquor at 20° Tw., | 1 | " |

*Blue, Dark (Cylinder)*—

| | | |
|---|---|---|
| Water, | 3½ | gals. |
| Starch, | 7 | lbs. |
| Sal-ammoniac, | 1 | lb. 6 ozs. |

Boil, and add whilst still hot—

| | | |
|---|---|---|
| Yellow prussiate, ground, | 6 | lbs. |
| Red prussiate, ground, | 3 | " |
| Tartaric acid, | 3 | " |

When quite cool, add—

| | | |
|---|---|---|
| Oil of vitriol, | 8 | ozs. |
| Oxalic acid, | 8 | " |

(Previously dissolved in 2 lbs. boiling water.)

| | | |
|---|---|---|
| Tin pulp (as below), | 3 | gals. |

To prepare the tin pulp make a concentrated solution of protochloride of tin (which may be done by dissolving tin crystals in the smallest possible quantity of water, and adding muriatic acid in just sufficient quantity to clear the solution), and add as much yellow prussiate in solution as will throw down all the tin as a prussiate. Wash by decantation, and drain on the filter to a stiff paste.

A *light blue* may be produced by adding to 1 gallon of the dark blue just given 3 gallons of gum substitute water at 4 lbs. to the gallon.

*Brown, Light*—

| | | |
|---|---|---|
| Brown standard (see below), | 2 | quarts. |
| Gum-water (4 lbs. per gall.), | 2 | " |
| Red liquor at 18° Tw., | ½ | pint. |
| Nitrate of copper, | 1 | " |

After printing let lie four nights, and run through a weak solution of arseniate of soda, heated to 180° Fahr. Wash in hot water, pass through very weak chloride of lime, and dry.

*Brown, Dark.*—The same colour as the above. After printing, steam for half an hour, age for two nights, wash off in a weak solution of bichrome, wash well, and dry

*Brown Standard* (as above mentioned)—

| | | |
|---|---|---|
| Cubic catechu, | 25 | lbs. |
| Water, | 32 | quarts. |

Boil for eight hours, and add—

| | | |
|---|---|---|
| Acetic acid, | 2½ | quarts. |

Then dissolve sal-ammoniac, 10 lbs., in water, 15 lbs. Mix both these liquids well, let them settle, draw off the clear liquid, and thicken with gum-water.

*Another Brown*—

| | | |
|---|---|---|
| Berry liquor at 3° Tw., | 2 | gals. |
| Peachwood liquor at 8° Tw., | 1 | " |
| Logwood liquor at 8° Tw., | ½ | pint. |
| Nitrate of copper, dry, | 3 | lbs. |
| Alum, | 3 | " |

*Buff*—

| | | |
|---|---|---|
| Madder liquor, | 1½ | gals. |
| Bark liquor at 10° Tw., | 2 | quarts. |
| Red liquor at 14° Tw., | 1 | gal. |
| Starch, | 3½ | lbs. |

Boil well, and add—

| | | |
|---|---|---|
| Crystals of tin, | 1 | oz. |

*Chocolate*—

| | | |
|---|---|---|
| Logwood liquor at 12° Tw., | 3 | quarts. |
| Sapan liquor at 12° Tw., | ½ | gal. |
| Nitrate of alumina (see below), | 1 | quart. |
| Bark liquor at 12° Tw., | 1 | pint. |
| Water, | 1 | gal. |
| Starch, | 4¼ | lbs. |

Boil, and add—

| | | |
|---|---|---|
| Chlorate of potash, | 2 | ozs. |
| Red prussiate, | 10 | " |

*Nitrate of Alumina* (referred to above)—

| | | |
|---|---|---|
| Boiling water, | 2 | gals. |
| Nitrate of lead, crystallized, | 6 | lbs. |
| Alum, | 6 | " |
| Soda crystals, | 1¼ | lb. |

Dissolve, let the mixture settle, and draw off the clear liquid for use.

*Cinnamon*—

| | | |
|---|---|---|
| Cochineal liquor at 8° Tw., | 2 | quarts. |
| Logwood liquor at 8° Tw., | 2 | " |
| Berry liquor at 10° Tw., | 2 | " |
| Alum, | 3½ | lbs. |
| Cream of tartar, | ½ | lb. |
| Starch, | 1 | " |

Boil, and while yet warm, add—

| | | |
|---|---|---|
| Tin crystals, | 6 | ozs. |

*Drab*—

| | | |
|---|---|---|
| Lavender liquor (see below), | 1 | gal. |
| Blue standard, | 1 | " |
| Bark liquor at 8° Tw., | 1 | quart. |
| Gum-water, | from 10 to 17 | gals. |

*Lavender Liquor* (above mentioned)—

| | | |
|---|---|---|
| Red liquor at 18° Tw., | 4 | gals. |
| Ground logwood, | 12 | lbs. |

Steep for 48 hours, and strain off the clear. To obtain a stronger quality increase the amount of logwood.

*Blue Standard* (above mentioned)—

| | | |
|---|---|---|
| Water, | 2 | gals. |
| Alum, | 1½ | lb. |
| Oxalic acid, | 9 | ozs. |
| Yellow prussiate, | 4½ | lbs. |
| Gum-substitute water, | 2 | gals. |

*Green* (cylinder work)—

| | | |
|---|---|---|
| Berry liquor at 12° Tw., | 7 | gals. |
| Yellow prussiate, | 15 | lbs. |
| Alum, | 8 | " |
| Gum-substitute, | 28 | " |

After boiling, add—

| | | |
|---|---|---|
| Tin crystals, | 2 | lbs. |
| Oxalic acid, | 2 | " |

Dissolve and stir well together.

*Green* (block)—

| | | |
|---|---|---|
| Yellow prussiate, | 14 | lbs. |
| Boiling water, | 3 | gals. |

Meanwhile mix in another vessel—

| | | |
|---|---|---|
| Water, | 1 | gal. |
| Double muriate of tin, 120° Tw., | 2 | quarts. |
| Gum Senegal water (6 lbs. per. gal.), | 5 | gals. |

Mix the two liquids thoroughly by pouring them backwards and forwards, and stirring the whole very carefully. When thoroughly mixed and clear, add—

| | |
|---|---|
| Berry liquor at 10° Tw., | 6 gals. |
| Tartaric acid, | 5 lbs. |
| Oxalic acid (dissolved in 2½ gals. water), | 1¼ " |
| Acetic acid, | 3 pints. |
| Extract of indigo, | 12½ ozs. mea. |

*Green for Blotch Grounds—*

| | |
|---|---|
| Bark liquor at 10° Tw., | 4 gals. |
| Starch, | 6 lbs. |

Boil well together, and add—

| | |
|---|---|
| Alum, | 2½ lbs. |
| Yellow prussiate, | 6 " |
| Tartaric acid, | 3 " |
| Oxalic acid, | ¾ " |
| Tin pulp, | 1 quart. |

Steam greens are frequently "raised," *i.e.*, brightened after printing, by passing through a weak solution of bichrome.

*Dark Grey—*

| | |
|---|---|
| Gum-water, | 2 gals. |
| Lilac standard (see below), | 1 " |
| Yellow prussiate, | 2 lbs. |
| Hot water, | ½ gal. |

*Lilac Standard—*

| | |
|---|---|
| Logwood liquor at 12° Tw., | 4 gals. |
| Red liquor at 18° Tw., | 4 " |
| Oxalic acid, | 2 lbs. |
| Sal-ammoniac, | 2½ " |
| Verdigris, crystallized, | 20 ozs. |

*Lavender—*

| | |
|---|---|
| Lavender liquor (see above), | 2 gals. |
| Blue standard (see above), | 2 " |
| Gum-water, to shade, | 12 to 24 gals. |

*Lilac—*

| | |
|---|---|
| Pink standard (see below), | 3 gals. |
| Purple standard (see below), | 1 " |
| Gum-water, | 3 " |

*Pink Standard—*

| | |
|---|---|
| Cochineal liquor at 6° Tw., | 2 gals. |
| Alum, | 1 lb. |
| Cream of tartar, | 1 " |
| Oxalic acid, | 4 ozs. |

This standard, thickened with 2 gallons of strong gum Senegal water, serves for a pink steam colour.

*Purple Standard—*

| | |
|---|---|
| Logwood liquor at 12° Tw., | 1 gal. |
| Alum, | 6 ozs. |
| Red prussiate, | 4 " |
| Oxalic acid, | 2 " |

If thickened with 4 gallons of gum-substitute water this mixture is a good steam purple for cylinder work. If for block work 6 gallons of gum-water are needed.

*Pink (Sapan)—*

| | |
|---|---|
| Sapan liquor at 3° Tw., | 1 gal. |
| Pink salt, | 1 lb. |
| Sal-ammoniac, | 8 ozs. |
| Oxalic acid, | 1 oz. |
| Blue vitriol, | 1 " |
| Thick gum-water, | 1 gal. |

*Pink, Cochineal—*

| | |
|---|---|
| Cochineal liquor at 8° Tw., | 2 gals. |
| Starch, | 2½ lbs. |

Boil a short time and add—

| | |
|---|---|
| Oxalic acid, | 6 ozs. |

Dissolve and strain. After printing steam for forty minutes at a pressure of 3 lbs., let lie over night, run through very weak alum water, and finish.

*Purple, Deep—*

| | |
|---|---|
| Logwood liquor at 16° Tw., | 2 gals. |
| Soda crystals, | ½ lb. |
| Red liquor at 20° Tw., | 2 gals. |
| Red prussiate, | 1 lb. |
| Oxalic acid, | 1 " |
| Gum Senegal, | 12½ lbs. |
| Sapan liquor at 8° Tw., | 1 gal. |
| Bark liquor at 12° Tw., | 5 ozs., mea. |
| Nitrate of alumina, | 25 " |
| Alum, | 10 " weight. |
| Chlorate of potash, | 1¼ " |
| Starch, | 1 lb. 14 ozs. |

*Stone-colour—*

| | |
|---|---|
| Lavender liquor, | 2 gals. |
| Blue standard, | 3 " |
| Black liquor at 12° Tw., | 2 quarts. |
| Gum-water, to shade, | 20 to 35 gals. |

*Full Yellow—*

| | |
|---|---|
| Berry liquor at 1° Tw., | 2 gals. |
| Flour, | 2½ lbs. |

Boil, and add—

| | |
|---|---|
| Alum, | 18 ozs. |

When cool, stir in

| | |
|---|---|
| Tin crystals, | 6 ozs. |

When all is dissolved, strain. After printing, steam for thirty minutes at 3 lbs. pressure, let lie one night, run through a weak solution of alum, and finish.

The coal-tar colours, certain extracts of madder, and the pigments are generally also fixed by the steaming process. The following are examples of their use:—

*Aloes Green—*

| | |
|---|---|
| Chrysammide, | 2 grms. |
| Gum-water to shade. | |

This mixture, after steaming, gives a pleasing moss green shade, not affected by boiling water or by madder or garancin becks. Thus a green design may be printed on, or a green ground may be padded in. Iron and alumina mordants may then in either case be blocked in, and the piece dyed up in the madder or garancin beck. Novel and pleasing effects may thus be obtained.

*Aloes Rose—*

| | |
|---|---|
| Gum-water, | 1 litre. |
| Chrysammic acid, | 2 grms. |

This mixture gives a rose on cottons, woollens, or silks without steaming on pieces previously prepared with stannate of soda. By steaming, the rose may be converted into a violet.

*Aurine Orange—*

| | |
|---|---|
| Aurine solution, | 8 ozs. |
| Lactarine thickening, | 1 gal. |

Mix well. To prepare the thickening take—

| | |
|---|---|
| Water at 80° Fahr., | 7 pints. |
| Ammonia, | 1 pint. |
| Lactarine, | 2 lbs. |

Stir till perfectly dissolved. After printing, steam for twenty minutes.

*Coralline Red—*

| | |
|---|---|
| Coralline, | 100 grms. |
| Alcohol, | 900 " |

Dissolve and add—

| | |
|---|---|
| Solution of caseine, | 2250 grms. |

To prepare this solution take :—

| | |
|---|---|
| Cascine, | 100 grms. |
| Water, | 300 " |
| Ammonia, | 20 " |

Stir till dissolved.

*Coralline Yellow*—Dissolve yellow coralline in dilute ammonia till the solution stands at 32° Tw. To 1 measure of this liquid take 4 measures of starch-paste, at 14 lbs. per gallon. After printing, dry and steam for one hour.

*Eosine Pinks and Roses*—Eosine may be applied in the same manner as aurine and coralline.

*Saffranin Pink*—Mix half a pint of saffranin paste with 10 pnts of the following thickening :—

| | |
|---|---|
| "Acetate of alumina standard," | 1 gal. |
| Water, | 1 " |
| Starch, | 2 lbs. |

After boiling cool, and add 1 pint of "arsenic and glycerine standard."

*Acetate of Alumina Standard* (above mentioned)—Boiling water, 2 quarts; alum, 20 ozs.; dissolve and add white sugar of lead, 1½ lb. Dissolve, settle, and take the clear for use.

*Arsenic and Glycerine Standard*—Boil 1 lb. arsenious acid in 1 quart glycerine till dissolved, and filter.

After the saffranine is printed, the pieces are steamed for thirty minutes.

*Aldehyde Green*—

| | |
|---|---|
| Gum-water, | 1 litre. |
| Paste green, | ¼ kilo. |
| Bisulphite of soda, | 150 grms. |

Dissolve in the water-bath, and let stand for three or four days before use. It may be steamed after printing, but it succeeds better upon animal fibres than upon calico.

*Garnet Brown*—

| | |
|---|---|
| Solution of magenta, 50 grms per litre of alcohol, | 25 centilitres. |
| Gum-water, | 75 " |
| Oxalic acid, | 50 grms. |
| Chlorate of potash, | 25 " |

*Aniline Grey*—

| | |
|---|---|
| Aniline grey (Gris Castelhaz), | 1 quart. |
| Reduction paste, | 1 gal. |

To prepare the reduction paste take :—

| | |
|---|---|
| Acetate of alumina, | 1 gal. |
| Water, | 1 " |
| Starch, | 3 lbs. |

Boil till dissolved, cool, and add—

| | |
|---|---|
| Arsenic and glycerine standard, | 1 pint. |

Mix well together. After printing, steam for thirty minutes.

The aniline colours in general, such as magenta, HOFMANN'S violet, &c., may be fixed upon calico in various methods. SCHULTZ mixes one quarter litre acetate of alumina at 10° B. with 20 grms. arsenite of soda per every 4 grms. of magenta, &c., employed, and thickens with starch which has been previously boiled to a paste separately, using the more thickening the lighter the intended shade. The colour is then added, and the pieces, after printing, are steamed.

Another process is to dissolve gelatine in the proportion of 50 grms. per litre of water. Solution of bichromate of potash is then very gradually added till the liquid is of a straw colour. The aniline dye is then added, and the mixture thickened with dextrine. After printing the goods are exposed for some hours to light, which renders the gelatine insoluble when in contact with chrome. Instead of gelatine lactarine may be used, dissolved in a little ammonia. It must be remembered that the action of light is apt to injure many aniline colours.

The most general method is to mix the colour with albumin or lactarine. The former is the more expensive of the two, but gives better results. For the lightest shades egg albumin is preferred, but for heavy shades blood albumin may be substituted. Both kinds are dissolved in *cold* water in proportions varying from about 8 lbs. down to 2 lbs. per gallon. It is scarcely needful to remark, that colours containing albumin must not be exposed to heat. After printing they are fixed by steaming.

The following examples may serve to illustrate this method :—

*Dark Magenta*—

| | |
|---|---|
| Fine flour, | 1 lb. |
| Palest British gum, | 8 ozs. |
| Water, | 2½ lbs. |
| Magenta liquor, | 1 pint to 1 1/10. |

Boil thoroughly, and when cold stir in 40 ozs. measure of egg-albumen solution at 8 lbs. to the gallon of water.

The magenta liquor is obtained by taking—

| | |
|---|---|
| Magenta crystals, | 10 ozs. |
| Methylated spirit (free from shellac), | 7 quarts. |
| White glycerine, | 1 quart. |
| Water, | 1 gal. |

*Dark Violet*—

| | |
|---|---|
| Water, | ½ gal. |
| Fine flour, | 4 lbs. |
| Palest British gum, | 2 lbs. |
| Strong solution of methyl-violet in spirit, | 5 quarts. |

Boil well, and after cooling add—

| | |
|---|---|
| Egg-albumen liquor, at 8 lbs., | ½ gal. |

The following are instructions for the use of artificial alizarin :—

*Red*—

| | |
|---|---|
| Alizarin paste (20 per cent.) | 2½ lbs. |
| Thickening, | 16 " |
| Red liquor at 15° Tw., | 1 lb. |
| Acetate of lime at 25° Tw., | ½ " |

The thickening is prepared as follows :—

| | |
|---|---|
| Wheat starch, | 12 lbs. |
| Water, | 10 gals. |
| Acetic acid at 9° Tw, | 1 gal. |
| Gum tragacanth, | 1¼ lb. |
| Olive oil, | 2 " |

Boil the whole well together, and stir till the mixture is quite cold.

*Pinks.*—The same colour as directed for reds, but diluted with 2 to 3 parts of thickening according to shade.

For styles where two reds are used, the deeper shade being printed on first, the goods are steamed one hour before the second printing. Afterwards they are again steamed for one hour, and aged for twenty-four hours, and passed through one of the subjoined baths at a temperature of 120° to 140° Fahr., not being left in the bath longer than from one to one and a half minute.

| | |
|---|---|
| Water, | 250 gals. |
| Chalk, | 60 lbs. |
| Tin crystals, | 3 " |

Or,

| | | |
|---|---|---|
| Water, | 250 | gals. |
| Chalk, | 40 | lbs. |
| Arseniate of soda, | 10 | " |

The pieces are then washed, and brightened or cleared as follows:—For 10 pieces of 50 yards each take—

1st. soaping at 120° Fahr., 3 lbs. soap, ¼ lb. tin crystals.
2nd. soaping at 160° Fahr., 3 lbs. soap.
3rd. soaping at 175° Fahr, 3 lbs. soap.

The pieces are washed between each soaping.

*Red for Mosaics—*

| | | |
|---|---|---|
| Alizarin paste at 10 per cent., | 8 | lbs. |
| Thickening, | 2½ | gals. |
| Nitrate of alumina at 23° Tw., | 9½ | ozs. |
| Red liquor at 15° Tw., | 19 | " |
| Acetate of lime at 25° Tw., | 13 | " |

Or,

| | | |
|---|---|---|
| Alizarin paste (10 per cent.), | 10 | lbs. |
| Thickening, | 2½ | gals. |
| Nitrate of alumina at 23° Tw., | 13 | ozs. |
| Red liquor at 15° Tw., | 19 | " |
| Acetate of lime at 25° Tw., | 16 | " |

*Red, without Oil—*

| | | |
|---|---|---|
| Alizarin paste (10 per cent.), | 8½ | lbs. |
| Acetic acid at 12 Tw., | 9½ | " |
| Wheat flour, | 3½ | " |
| Water, | 2½ | quarts. |

Boil well, and stir till quite cold, and then add—

| | | |
|---|---|---|
| Acetate of lime at 29° Tw., | 1 | lb. |
| Nitrate of alumina at 23° Tw., | 2 | " |
| Hyposulphite of lime at 13° Tw., | 3 | " |

*Purple—*

| | | |
|---|---|---|
| Alizarin paste (10 per cent.), | 3 | lbs. |
| Purple thickening, | 2½ | gals. |
| Pyrolignite of iron at 18° Tw., | 6 | ozs. |
| Red liquor at 25° Tw., | 12 | " |

*Thickening for Purples—*

| | | |
|---|---|---|
| Starch, | 19 | lbs. |
| Water, | 10 | gals. |
| Acetic acid, | 3 | quarts. |
| Gum tragacanth, | 1½ | lb. |
| Olive oil, | 2 | " |

Boil well together, and stir till quite cold.

*Brown—*

| | | |
|---|---|---|
| Alizarin paste at 15 per cent., | 13¼ | lbs. |
| Thickening, | 2¼ | gals. |
| Nitrate of alumina at 29° Tw., | 2 | lbs. |
| Red liquor at 19° Tw., | 15 | ozs. |
| Red prussiate of potash, dissolved in water, | 15 | " |
| Acetate of lime at 29° Tw., | 17 | " |

If a yellower shade is required, add to every quart of the mixed colour 1 oz. of bark liquor at 20° Tw. Red colours which are spoiled or too old may be conveniently used as browns by adding per quart of mixed colour ¾ oz. to 1 oz. of red prussiate, dissolved in water.

The mordants used in the above artificial alizarin colours are prepared as follows:—

*Red Liquor.*—Stir into 6 quarts of acetic acid 30 lbs. hydrate of alumina, warm, filter, and let down with water to the specific gravity required.

The hydrate of alumina is obtained by dissolving separately 72 lbs. of alum and 62 lbs. soda, each in 100 gallons of water. Mix the two solutions, wash the precipitate eight times by decantation, collect it on a filter, and press it. It must be dissolved before it gets dry.

*Nitrate of Alumina—*

| | | |
|---|---|---|
| Nitrate of lead | 2 | lbs. |
| Alum. | 2 | lbs. |
| Water, | ½ | gal. |

Dissolve the ingredients, mix, filter off the clear liquid from the precipitate, and dilute to the strength required. Nitrate of alumina gives a yellower red than does red liquor, and when it is used more acetate of lime is required.

*Acetate of Lime.*—A solution of acetate of lime at 25° Tw. contains one-fourth its weight of the dry substance. One-tenth of the weight of the alizarin paste is generally required. With fresh qualities of artificial alizarin it is best to determine the amount needed by an experiment on a small scale.

*Dark Red from Artificial Alizarin—*

| | | |
|---|---|---|
| Alizarin paste at 10 per cent., | 12 | lbs. |
| Wheat starch, | 7 | " |
| Acetic acid at 80° Tw., | 2½ | " |
| Gum tragacanth mucilage (1 lb. per gallon), | 1 | lb. |
| Acetate of lime at 80° Tw., | 1¼ | gal. |
| Water, | 2 | " |
| Olive oil, | ½ | " |
| Boil well, let cool, and add red liquor at 11° Tw., | 10 | quarts. |

The red liquor here specified is made by dissolving 4 lbs. alum and 4 lbs. sugar of lead in 4 quarts of water, and taking the clear liquid.

*Another Dark Red—*

| | | |
|---|---|---|
| Alizarin paste at 10 per cent., | 1 | quart. |
| Acetic acid at 12° Tw., | 15 | oz. (meas.) |
| Starch paste at 2 lbs. per gallon, | 3½ | pints. |
| Acetate of lime at 20° Tw., | ½ | " |
| Red liquor (as in last receipt), | 12½ | oz. (meas.) |
| Olive oil, | ½ | pint. |

*Light Red—*

| | | |
|---|---|---|
| Alizarin paste (from MEISTER, LUCIUS, and BRÜNING), at 10 per cent. | 2¾ | quarts. |
| Acetic acid at 12° Tw., | 1½ | " |
| Starch paste at 2 lbs. per gallon, | 8¼ | " |
| Acetate of lime at 20° Tw., | 1 | " |
| Red liquor as above, | 1¼ | " |
| Olive oil, | 3 | pints. |

*Purple—*

| | | |
|---|---|---|
| Artificial alizarin as in last receipt, | 2 | lbs. |
| Acetic acid at 8° Tw., | 1 | pint. |
| Gum-gedda water at 4 lbs per gal. | 7 | " |
| Black liquor at 10° Tw., | ½ | " |
| Acetate of lime at 20° Tw., | ⅛ | " |

The following method may be used for the production of a shade resembling turkey red from artificial alizarin. The paste colour, containing 25 per cent. of dry material, is dissolved in five times its weight of spirit, and the solution is at once mixed with a strong solution of muriate of alumina, the pure chloride of aluminium in which should be equal in weight to one-third of the colouring matter. The mixture is then thickened as needful with mucilage of gum tragacanth. To every half litre of the solution is then added 30 cubic centimètres of a solution of best olive oil in sulphuric acid, and alcohol in the proportions of 15 : 1 : 15, and very well stirred in.

The colour must be as thin as possible, so as not to run. The pieces before being printed with this colour are first prepared with red liquor at about 8° B., dried and exposed to the air for two days, passed through a soap-beck made up with 30 grms. of Marseilles soap per litre of water, washed well, and dried. After printing the goods are steamed at a moderately high pressure in ammoniacal steam, passed through a weak soap-beck, washed in a current of water, and brightened by passage through the following solutions :—1. Cold nitric acid sours, 3 cubic centimètres of acid to 1 litre of water. 2. Wash in current of water. 3. Cold nitric acid sours, 5 cubic centimètres per litre. 4. Half a grm. tin crystals per litre, water at 30° C. 5. Wash in current of water. 6. 15 cubic centimètres of chloride of soda at 8° B. per litre of cold water. 7. Thorough washing. The shade is now thoroughly developed, and resists light, air, and soap-lyes like a turkey red.

The muriate of alumina used in this process is made by mixing sulphate of alumina with chloride of barium, an excess of the latter being carefully avoided. The mixture is allowed to settle, and the clear liquid is run off from the sediment.

Natural alizarin, and other improved preparations of madder now in the market, are fixed upon the fibre in the same manner as artificial alizarin.

*Pigment Colours*, which now play a very important part in printing, and are made to produce some very beautiful effects, are generally mixed with albumin, lactarine, or gluten, and steamed after printing. The following are examples of a few of the principal of these colours :—

*Ultramarine Blue—*

| | |
|---|---|
| Water, | 7 pints. |
| Lactarine, | 3 lbs. |

Stir up well, and add—

| | |
|---|---|
| Ammonia. at sp. gr. 0·88, | 5 ozs. meas. |
| Soda lye (caustic) at 32° Tw. | 10 ozs. |

Meantime work up

| | |
|---|---|
| Ultramarine, | 6 lbs. |
| Water, | 2½ pints. |

And mix with the other ingredients.

*Ultramarine Blue with Albumin—*

| | |
|---|---|
| Ultramarine, | 2 lbs. |
| Water, | 1 pint. |
| Gum tragacanth water at 10 ozs. per gal. | 1 pint. |
| Egg-albumin liquid at 8 lbs. per gal. | 1 quart. |

*Green* (GUIGNET'S)—Grind up 13 lbs. of GUIGNET'S paste green with 1 gallon of blood albumin solution at 3 lbs. per gallon, add to it when thoroughly smooth 1 gallon more of the same solution.

In like manner scarlets are produced with vermillion and ultramarine, grey with lamp-black, orange with chromates of lead, browns with burnt sienna, ultramarine, and ochre, the finest roses with ordinary cochineal carmine, &c. It must be remembered that no acids or acid vapours should be allowed to come in contact with ultramarine work.

*Aniline Black.*—We may here append a notice of aniline black, one of the most valuable and interesting improvements ever introduced into the art of calico printing. This black, originally invented by the late Mr. J. LIGHTFOOT of Accrington, is unattacked by soap or by the action of light. Strong acids turn it to a dark green, but alkalies restore the black in its original fulness. Chloride of lime turns it a deep brown; but here again the colour may be brought back by washing with water. It can be printed along with madder colours, steam colours, &c., thus producing a variety of novel effects.

The following process was patented by the inventor in 1871 :—

| | |
|---|---|
| Chocolate paste, | 1 gal. |
| Basic muriate of aniline, | 48 ozs. meas. |
| Sulphide of copper, | 1 pint. |

To make the basic muriate of aniline, take—

| | |
|---|---|
| Aniline oil, | 4 quarts. |
| Best muriatic acid at 34° Tw., | 3 quarts. |

And mix well together.

To prepare the sulphide of copper, take—

| | |
|---|---|
| Flowers of sulphur, | 2 lbs. 2 ozs. |
| Caustic soda at 70° Tw., | 11½ lbs. |

Stir well till dissolved, but without applying heat, and add it to sulphate of copper, 10 lbs., previously dissolved in 20 gals. boiling water. Wash by decantation till the washings are neutral to test-paper, and strain till the bulk of the pulp is reduced to 1 gal. For the chlorate paste, take—

| | |
|---|---|
| Water, | 10 gals. |
| Wheat starch, | 23 lbs. |
| Sal-ammoniac, | 5½ lbs. |
| Chlorate of potash, | 4 lbs. |
| Solution of chlorate of soda, as below, | 2 gals. |

Boil and cool.

The solution of chlorate of soda is prepared from—

| | |
|---|---|
| Caustic soda, at 70° Tw., | 1 gal. |
| Tartaric acid, | 7½ lbs. |
| Previously dissolved in water | 3¾ gals |
| Heat to 170° F., and add chlorate of potash, | 12 lbs. |
| Dissolve and add a solution of tartaric acid, | 7½ lbs. |
| In water, | 6½ quarts. |

Stir till cold, strain, press the sediment with a board on which weights are laid. Stir it up again with 6 quarts of cold water, strain and press again, and mix the filtered liquors, which are then set at 28° Tw.

KŒCHLIN boils together :—

| | |
|---|---|
| Water, | 10 litres. |
| Starch, | 2 kilos. |
| Calcined starch, | 2 " |
| Aniline, | 2 " |
| Sal-ammoniac, | 4 " |
| Chlorate of potash, | 1 " |

When about to be used, add cold—

| | |
|---|---|
| Sulphide of copper paste, | 1 " |
| Tartaric acid, | 2 " |

As a general rule, it must be observed that the sulphide of copper, or any other compound used in its stead, should only be added immediately before printing. Salts of cerium have been proposed as a substitute for copper, and found to give even superior results, but their high price will probably prevent their practical application.

The following French receipt has been extensively useful :—

Dissolve 300 grms. starch in 2 litres of water,

150 grms. gum tragacanth in another 2 litres, and 750 grms. of light torrefied starch in a third 2 litres. Equal weights of these three solutions are then mixed together, adding, with the aid of heat, chlorate of potash to the extent of $\frac{1}{30}$ or $\frac{1}{40}$ the weight of this solution, and twice as much muriate of aniline as chlorate of potash. When the colour is going to be used add sulphide of copper equal in weight to the chlorate of potash.

Aniline blacks are not dried hard after printing, except when basic salts of ammonia are used, but merely enough to prevent the colour from smearing. They are then hung up for twenty-four hours at a temperature of 70° Fahr., with about 8° difference between the wet and dry bulb thermometers.

If the aniline black is the only colour printed on the goods the colour is raised by passing through boiling soap-lye, or through a carbonate of soda beck, 2 ozs. per gallon, at 160° Fahr., or through milk of lime. If a browner tone is required they are passed through a weak and hot bichromate of potash beck.

If the aniline black is accompanied with steam-colours the pieces are passed through ammonia *after* the ageing process, but *before* steaming. When aniline black is accompanied by the mordants for madder work it is sufficiently raised by the dunging process.

For preparing aniline blacks, Hartmann advises the use of samples of aniline which boil at from 180° to 185° C. Such as boil above 192° C. are found to give dirty browns.

A recent suggestion is the use of the ferrocyanide and ferricyanide (prussiates) of aniline instead of the muriate.

Printing Woollen Stuffs.—The great attraction which the fibre of wool has for colouring matters enables the printer to dispense with the preliminary mordanting which is in general given to calicoes, even to preparing them for steam-colours. The greatest care, however, is required in the bleaching or sulphuring of the wool, and more especially in the *azuring* which constitutes a part of that process. If salts of copper or tin are present, these will infallibly combine, under the action of the steam, with the sulphur adhering to the wool, unless it has been bleached in the most perfect manner, and spots or discolorations will be found after the steaming, which will be ruinous to the whole process. (See Bleaching.)

Chevreul has clearly established that these spots or stains are generally due to the presence of a compound of copper, or, more rarely, to that of a compound of tin with the sulphur of the wool, and that these stains are developed during the steaming, by the mutual action of the wool and a salt of copper in presence of steam.

The quality of the sulphate or acetate of alumina, which is the base of many steam-colours, must also be taken into consideration. Sometimes ordinary alum is used, sometimes acetate of alumina; and though it is of little importance in the printing of calicoes whether the acetate of alumina has been prepared directly, or by the double decomposition of alum and acetate of lead, it is different in the printing of woollen goods; for that which is derived from the acetate of lead *always retains a certain quantity of the sulphate of lead*, which, according to the nature of the colour, may act on the wool, and give it a brown tint, by reason of the sulphur which it contains.

The principal difference between the printing of woollen and cotton goods consists in the composition of the colouring mixtures applied. The woollen fibre resists the action of acids better than cotton, and hence in the mixtures for steam-colours for woollen goods a greater proportion of free acid is introduced, which has the effect of dissolving the lake, or the oxide of the mordant, and thus of producing a more intimate and a more uniform fixation, imparting at the same time a higher lustre to the shades. It is for this reason that in mixing steam-colours for woollens, a considerable quantity of tartaric or oxalic acid is almost always employed, whether the mordant mixed with the colour is perchloride of tin, protochloride of tin, or alum. At the same time, it is certain that even insoluble bodies, such as charcoal powder, often adhere firmly to wool, and dye it a durable and brilliant colour without undergoing solution. The most vivid colours on wool are generally obtained by protochloride of tin, with either oxalic or tartaric acid. To show the composition of the mixtures for such colours, a few examples may be given.

The *reds* for woollen stuffs are all formed with cochineal and preparations of tin. Thus for a poppy-red, take 1 gallon of cochineal liquor, made with 2½ lbs. of pulverized and prepared cochineal; thicken, hot, with 1¼ lb. of starch, and while still tepid add half a pound of oxalic acid, and 1 lb of a composition formed by adding 2 ozs. of tin to 9 ozs. of hydrochloric acid mixed with 5 ozs. of nitric acid.

For a *fine red*—boil for five minutes in 1 gallon of water 5 lbs. of crushed cochineal; thicken with half a pound of starch, and when the mixture has been well boiled, withdraw it from the fire and dissolve in it 1 lb. of oxalic acid and 10 ozs. of gum arabic; when cold, add 7 ozs. of chloride of tin at 106° Tw.

*Steam-yellows* for woollens are formed like the yellows for calico, by decoctions of Persian berry, quercitron, or weld, and have generally the oxide of tin along with alumina for their base. Thus, for an orange yellow, take 1 gallon of decoction of Persian berries at 14° Tw.; thicken with 2 lbs. of starch, and add to the mixture 10 ozs. of alum, 8 ozs. of chloride of tin, and 2½ ozs. of oxalic acid.

Two kinds of *blue* are in use for printing on woollen stuffs; the one formed with soluble indigo; the other with the ferrocyanide of potassium. Both have alumina for their base, and to promote its solution not only oxalic acid, but likewise a certain proportion of tartaric acid is introduced. To fix Prussian blue on wool, the red cyanide is decomposed by a suitable proportion of tartaric acid to set free the cyanide of iron, and a preparation of tin is added, the object of which is not so much to fix the colour, as to give it that fine shade known by the name of *royal blue*.

For a good *indigo blue*, dissolve in 1 gallon of warm water 5 ozs. of the soluble indigo of commerce; thicken with 3½ lbs. of gum, add 4 ozs. of alum, 5 ozs. of oxalic acid, and 3 ozs. of tartaric acid.

For a *Prussian blue*, in 1 gallon of water dissolve 12 ozs. of alum and 1 lb. of oxalic acid; thicken with 7½ lbs. of gum, then add to the tepid mixture half a pound of chloride of tin, 2½ lbs. of ferrocyanide of potassium, and 12 ozs. of nitrate of iron at 76° Tw.

Woollen goods are sometimes steamed at two operations, to prevent the flowing of the colours by a too prolonged exposure; but goods printed with detached figures are generally exposed to a single steaming of forty or fifty minutes' duration. The washing and dyeing of the woollen stuffs, after being printed and steamed, are two operations requiring some management. The ordinary washing machines soak the goods too much, and render the subsequent drying too slow. The best method is to subject the goods to a rapid wincing in a bath fitted with a reel like that of the ordinary dye beck, and capable of receiving a very rapid motion. The goods are then rapidly dried by means of the hydro-extractor.

DELAINES.—The printing *delaines*, which are formed of a mixture of cotton and wool, presents greater difficulty than is involved in the printing of either of the fibres separately. This will be obvious from the fact that the composition or mixture of the colours which is most suitable for cotton is less adapted for wool, and, on the other hand, the quantity of acids which is put into the colour mixtures intended for printing on pure woollens, would in many cases burn or injure the cotton fibre. There are some colours, also, easily fixed on wool, but which have very little adherence to cotton stuffs; and as a general rule it must be obvious that the greater attraction of the woollen fibre for the colouring matters must tend to create an inequality of shade in the colour or colours imparted to the two materials composing the printed stuff. The sulpho-indigotate of potassium, or soluble blue of commerce, affords a striking example of a colour which, when printed on delaines, communicates a strong shade to the wool, but only an imperfect coloration to the cotton contained in the fabric; and the mode in which this inequality is corrected will show how the difficulty is surmounted in most cases. It consists in mixing with the indigo blue for the wool a suitable proportion of steam blue for the cotton, prepared by a mixture of yellow or red prussiate of potash with tartaric, oxalic, or sulphuric acid, and alum. In one peculiar style of fancy dyeing, the woollen thread only is dyed, and the cotton is afterwards perfectly bleached by exposing the dyed delaines to a dilute solution of bleaching powder.

Delaines for printing are now generally prepared in the following manner:—After being thoroughly bleached the pieces are twice padded in stannate of soda, in a machine with wooden rollers. Next they are winced through sulphuric acid sours at 3° Tw., washed slightly, dried imperfectly, and then twice padded in sulpho-muriate of tin at 4° Tw.

The sulpho-muriate of tin is prepared by taking

| | |
|---|---|
| Double muriate of tin at 120° Tw., | 3 quarts. |
| Sulphuric acid, full strength, | 2 " |

Mix gradually, and add an equal measure of ordinary muriatic acid at 32° Tw.

After padding the pieces are run at once into a large beck fitted with rollers, and containing chloride of lime solution at ½° Tw. They are then washed, whizzed, and dried. Just before printing they are padded in gum Senegal water, half a pound per gallon, and dried again.

The steaming is performed in the same manner as for woollens, and either by the column or chamber, but generally for three quarters of an hour only. This is a point, however, for which it is impossible to lay down any fixed rule, as the time must vary according to the manner in which the steam is applied, the dimensions of the chamber, and the quantity of acid in the mixtures. With a considerable quantity of acid, such as is best adapted for woollen stuffs, the fibres of the cotton especially become weakened by too long exposure.

As specimens of the colours used for delaines we may take the following:—

*Black—*

| | |
|---|---|
| Logwood liquor at 12° Tw., | 6 quarts. |
| Starch, | 1½ lbs. |

Boil together, and when it has cooled down to 90° F. add—

| | |
|---|---|
| Nitrate of iron at 86° Tw., | 1 pint. |

*Royal Blue—*

| | |
|---|---|
| Water, | 2 gals. |
| Starch, | 5 lbs. |
| Solution of red prussiate at 30° Tw., | 2 gals. |
| Gum tragacanth water, | 1 quart. |

Boil and add—

| | |
|---|---|
| Tin pulp, | 6 quarts |
| Tartaric acid, | 36 ozs. |
| Oxalic acid, | 6 " |

Add, when cold—

| | |
|---|---|
| Yellow prussiate, | 8 lbs. |
| Tartaric acid, | 10 " |

*Brown—*

| | |
|---|---|
| Sapan liquor at 9° Tw., | 2 quarts. |
| Berry liquor at 18° Tw., | 2 " |
| Archil liquor at 12° Tw. | 1 " |
| Starch, | 1 lb. |

Boil and add—

| | |
|---|---|
| Alum, | 12 ozs. |
| Sal-ammoniac, | 2 " |
| Verdigris, | 1 " |

*Chocolate—*

| | |
|---|---|
| Sapan liquor at 20° Tw., | 1 gal. |
| Nitrate of alumina, | 1 " |
| Logwood liquor at 30° Tw. | 3 pints. |
| Bark liquor at 30° Tw., | 1 quart. |
| Ground gum, | 14 lbs. |
| Chlorate of potash, | 10 ozs. |

Dissolved in—

| | |
|---|---|
| Boiling water, | 3 quarts. |
| Blue vitriol, | 3 ozs. |

*Green—*

| | |
|---|---|
| Berry liquor at 12° Tw., | 2 gals. |
| Alum, | 1½ lbs. |
| Starch, | 3 " |

Boil and add—

| | |
|---|---|
| Ground yellow prussiate, | 3 lbs. |
| Tin crystals, | 8 ozs. |
| Oxalic acid, | 8 " |
| Extract of indigo (measure), | 37 " |

*Orange*—

| | |
|---|---|
| Bark liquor at 19° Tw. | 1 quart. |
| Starch, | 10 ozs. |
| Water (measure) | 25 " |

Boil and add—

| | |
|---|---|
| Cochineal liquor at 8° Tw., | ½ pint. |
| Tin crystals, | 4½ ozs. |

*Pink*—

| | |
|---|---|
| Ammoniacal extract of cochineal at 10° Tw., | 1 gal. |
| White tartar, | 2 ozs. |
| Alum, | 8 ozs. |
| Gum, | 4 lbs. |

*Scarlet*—

| | |
|---|---|
| Cochineal liquor at 12° Tw., | 1 gal. |
| Starch, | 2 lbs. |

After boiling add—

| | |
|---|---|
| Oxalic acid, | 2 ozs. |
| Salt of sorrel, | 2 " |
| Pink salt, | 4 " |
| Tin crystals, | 4 " |

*Yellow*—

| | |
|---|---|
| Berry liquor at 10° Tw., | 2 gals. |
| Starch, | 2 lbs. 10 ozs. |
| Pale British gum, | 8 ozs. |
| Tin crystals, | 14 " |

*Iodine Green*—

| | |
|---|---|
| Acetic acid, | 3 pints. |
| Gum gedda solution, | 6 quarts. |
| Solution of blood albumin (6 lbs. per gallon), | 4 gals. |
| Arsenical glycerine, standard, | 3 pints. |
| Iodine paste green, | 2 quarts. |

*Violet*—

| | |
|---|---|
| HOFMANN'S or methyl violet, dissolved in spirit, | 20 ozs. |
| White gum liquor (3 lbs.), | 3½ quarts. |
| Blood albumin liquor (6 lbs.), | 1 pint. |

The delaines, after printing, are hung up to cool, steamed, and after steaming, washed, whizzed, dried at a steam heat, and hung for a day or two in a cool room. Preparatory to steaming a piece of grey calico, previously padded in a weak beck of sugar of lead and dried, is wound on the reel along with each piece of delaine, to absorb any sulphur compounds liberated from the wool, and prevent stains.

PRINTING ON SILK STUFFS AND CHALIS.—The printing of steam colours on silks is similar to printing on woollens, except that the acids must be used more sparingly.

The madder style is only partially applicable to silks. Red, blacks, and chocolates are produced by a method closely analogous to that applied to calico, the mordants being printed on, aged, and dunged, and the goods after dyeing being soaped and washed in the usual manner. Purples do not succeed.

Silks are generally, however, printed in the steam-style, in which the whites retain their lustre unimpaired. The pieces are first prepared by steeping about four hours in a weak bath of sulpho-muriate of tin, generally at 2° Tw. This mordant is less acid than that used for delaines, being prepared by dissolving 1 lb. of tin crystals in water, adding very gradually 1 lb. of sulphuric acid at full strength, and letting down with water to the strength required.

The silks before steeping are boiled for about two hours with neutral curd soap, to the amount of 1 lb. for every 4 lbs. of goods. After the treatment with sulpho-muriate of tin, the pieces are washed in pure water and dried. The colours are generally similar to those used for woollens, but they require less acid, and a less amount of thickening. None of the gum substitutes or artificial gums should be used in silk printing, as they leave a harsh feel. Steam is generally applied at a rather low pressure for about half an hour.

As examples of the colours for silks we give :—

*Black*—

| | |
|---|---|
| Logwood liquor at 14° Tw. | 1 gal. |
| Starch, | 10 ozs. |
| Gum, | 1 lb. 10 ozs. |

Boil, and when cold add—

| | |
|---|---|
| Nitrate of copper (crystals) | 10 ozs. |
| Nitrate of iron, | 8 " |

*Blue.*—The royal, logwood, and indigo blues are almost entirely superseded by the aniline blues, which show to the greatest advantage upon silks. The spirituous solution of the colour is thickened with gum Senegal water, at 3 lbs. per gallon, using more or less according to shade. No albumin or lactarine is required, as the colour has a strong affinity for silks.

*Chocolate*—

| | |
|---|---|
| Sapan liquor at 12° Tw., | 1 gal. |
| Logwood liquor at 12° Tw. | 5 pints. |
| Dark liquor at 15° Tw. | 1 pint. |
| Sal-ammoniac, | 12 ozs. |
| Alum | 1 lb. |
| Gum Senegal, | 7 lbs. |

*Green, Dark*—

| | |
|---|---|
| Berry liquor at 14½° Tw., | 2 quarts. |
| Gum, | 1 lb. |

Dissolve and add—

| | |
|---|---|
| Extract of indigo, | 3¾ ozs. |
| Solution of tartaric acid at 36° Tw., | 2 " |
| Oxymuriate of tin at 80° Tw., | 1 " |

In greens, however, the methyl and iodine greens have nearly superseded all others, as they retain their tone by artificial light. They are fixed by the process of SEVEZ, as given for cotton, but are much more satisfactory upon silk. If a yellow shade is required, picric acid may be added.

*Orange* (coralline)—

| | |
|---|---|
| Corallinc, | 2 kilos. |

Add soda lye at 10° B., enough to dissolve it; dilute with water, add proto-chloride of tin (double muriate) at 40° B., apply heat, and filter. The precipitate thus obtained is mixed with

| | |
|---|---|
| Magnesia, | 100 grms. |
| Oxalic acid, | 260 " |
| Gum, ground, | 2000 " |

Water enough to make up 10 litres.

The whole is mixed well, heated, and strained. After printing it is then hung up for ten hours, and then steamed for thirty to forty-five minutes.

*Pink*—

| | |
|---|---|
| Sapan liquor at 6° Tw., | 2 gals. |
| Ground gum, | 6 lbs. |
| Bichloride of tin at 120° Tw., | 8 ozs. |

The finest pinks, and light roses upon silks, are produced by means of saffranin, no mordant being required.

*Purple*—

| | |
|---|---|
| Logwood liquor at 3 Tw., | 2 quarts. |
| Peachwood liquor at 3 Tw., | 2 " |
| Alum, | 2 lbs. |
| White sugar of lead, | 1½ " |

Much superior purples and violets are obtained with the aniline violet, Hofmann's, Perkin's Britannia, the methyl, &c. For a so-called *dark primula* 1 pint of the solution of Hofmann's violet is let down with 20 pints of gum Senegal water, at 3 lbs. per gallon. For paler shades a proportionately larger volume of gum-water is taken.

*Red*—

| | |
|---|---|
| Cochineal liquor at 4° Tw., | 1 gal. |
| Bark liquor at 12° Tw., | ½ pint. |
| Starch, | 1 lb. |

Boil, and after cooling add—

| | |
|---|---|
| Oxalic acid, | 5 ozs. |
| Tin crystals, | 5 " |

*Magenta, Deep.*—1 pint of Brock, Simpson, and Spiller's roseine (No. 2), and 6 pints of gum Senegal water (3 lbs.). For lighter shades increase the gum-water.

*Scarlet*—

| | |
|---|---|
| Cochineal liquor (strong), | 1½ gals. |
| Starch, | 1 lb. |

After boiling add—

| | |
|---|---|
| Fustic liquor at 15° Tw., | 2 ozs. |
| Berry liquor at 15° Tw., | 2½ " |
| Salt of sorrel, | 7 " |
| Tin crystals, | 1¼ " |
| Bichloride of tin at 100° Tw., | 5¼ lbs. |

*Yellow*—

| | |
|---|---|
| Water, | 2 gals. |
| Turmeric, | 3 lbs. |
| Berries, | 3 " |

Boil down to 1 gallon, strain, and add—

| | |
|---|---|
| Tin crystals, | ¼ lb. |
| Alum, | ½ " |
| Gum, more or less, | 2 " |

The steam-colours for chalis, or mixed fabrics of wool and silk, are necessarily similar to those applied to silks individually, because, if the acids were present in a free state, and in the same proportion with which they are mixed with wool colours, the texture of the silk in the fabric could not fail to be weakened. When this precaution is taken the printing of mixed fabrics of silk and wool, both of which are animal fibres and have nearly the same affinity for the colouring matters, is not attended with the same difficulty as that of delaines, or a mixture of wool and cotton.

**Dyeing Processes.**—Before proceeding to give a series of practical receipts for producing the various colours upon animal and vegetable fibres, and for the requisite subsidiary operations, a few general remarks will be useful.

Wool may be taken as the type of the animal fibres which come under the hands of the dyer. It contains nitrogen and sulphur, both of which have been supposed to play an important part in determining its relation to colouring matters. Its affinities for dyes, whether natural or artificial, are strong. Thus, it takes up without any mordant the bulk of the coal-tar colours, the preparations of archil, sulphate of indigo, &c. Even the so-called adjective colours, which require the aid of a mordant, stain it to a certain extent, though not with the fulness and body required to constitute a true dye. Wool is generally dyed in acidulated liquids, and at temperatures at or near 212° Fahr. But though little affected by dilute acids, it is readily injured by alkaline solutions, especially if hot; nor can it, as a rule, take up either mordants or colouring matters from alkaline solutions.

The principal mordants used in woollen dyeing are—alum, from which wool is able at a boiling heat to take a portion of alumina; bitartrate of potash (argol or tartar) is generally used as an adjunct to alum and the salts of tin, which it renders more easily decomposable by the fibre. The chromates of potash are very important mordants; and along with logwood and astringents form the greater part of the black dyes now used upon woollens. Iron is little employed as acetate or nitrate, but frequently as copperas. The preparations of tin used in woollen dyeing are chiefly protosalts; the protochloride, which in its different stages of concentration forms the single and double muriates of tin and tin crystals, being the chief. It is mixed in various proportions with sulphuric, tartaric, and oxalic acids, to subserve special purposes, and is sold under a variety of fanciful names.

Persalts of tin, commonly called oxymuriate, permuriate, nitro-muriate, and the like, are but little used by woollen dyers. The sesquisalt, known for want of a better name as nitrate of tin, is frequently employed, especially for scarlets and other cochineal colours. Here, more than in the case of cotton, the result of the coal-tar colours has been to diminish the scope for metallic mordants. The astringents, galls, catechu, sumach, &c., which play so important a part in cotton and even silk dyeing, have here no place. Mineral colours, properly so-called, such as chrome yellows, manganese browns, and iron buffs, are not employed in wool dyeing, and if attempted, give utterly unsatisfactory results. Even Prussian blues upon wool are produced, not by working the goods alternately in solutions of iron and of prussiate of potash (as in case of cotton and silk), but by heating in a solution of the latter substance in presence of an acid mixture known as "royal blue spirits."

Indigo is very extensively applied to wool in the vat. But the vats required for dyeing animal fibre are different in their composition from that used in cotton dyeing, and much more difficult to manage. The vats for wool are kept warm, whilst the cotton vat is worked at the ordinary temperature, and is hence spoken of as the "cold vat."

The affinity of wool for many colouring matters being very strong, there is often a difficulty in preventing them from working on to the fibre too

quickly, and in consequence irregularly. To prevent this substances are added to moderate the excessive affinity of the colours for the fibre. Of these substances, known as "levellers," the sulphate of soda is the most generally useful. In some cases a level shade is obtained by the mode of manipulation. The pieces are made to pass through the dye beck with very great velocity. Sometimes also the entire amount of colour necessary to dye a given weight of materials is not put into the beck at once, but added by degrees, the goods being of course withdrawn from the liquid at every such addition.

The colours of woollens are generally expected to be faster and more permanent than those of cotton tissues. During the process of manufacture many woollens are exposed to the operation of fulling or milling—in principle, severe friction and percussion in concentrated soap-lyes. When they pass into the hands of the consumer, they are expected to retain their colour and lustre longer than cotton wares, whilst exposed to air, sunshine, damp, perspiration, and other colour-destroying influences.

Wool comes into the hands of the dyer in its unwashed state, as yarn, and as pieces. Each of these conditions necessitates variations in the plant and manner of working, and to some extent also in the mixture of the dye wares. Each of them also has its especial advantages and its peculiar difficulties. A large quantity of wool is dyed loose in its unmanufactured state, though freed, of course, from all grease and dirt. This kind of dyeing is performed in large fixed pans, which according to the colour to be produced, and the materials to be employed, may be made of iron, copper, or block-tin. Provision is always made for the application of heat, either by a small furnace directly beneath the pan, or by means of steam blown into the liquid by a pipe pierced full of holes. When steam heat is used, metal pans may be replaced by stone, slate, or wooden cisterns. The mass of wool is duly turned about in the liquid with the dyers' pole, no mechanical arrangement having been yet devised to supersede manual labour in this department. Each of the two methods of heating has its disadvantages. The open fire beneath the dye pan may char a portion of the wool or of the dye wares that come in contact with the sides of the pan, just above the surface of the liquid. On the other hand, a current of steam rushing into the pan or cistern may under certain circumstances produce a regular rotatory motion of the wool which promotes felting; in other words, which causes the fibres of the wool to adhere together in a compact mass, not to be separated without injury to the quality and great labour.

Wool dyeing is considered on certain grounds preferable to yarn and piece dyeing. Every fibre of the wool is brought equally and thoroughly in contact with the dye liquor, no part being shielded by others. Hence the shades produced, other things being equal, are more solid and permanent. Hence, especially for goods which are required to resist considerable wear and tear, wool-dyed qualities are in demand, and fetch a higher price. If wool-dyed cloth is cut, the section will show the same depth of colour as the outer surface, which is not necessarily the case in piece-dyed goods. Wool-dyed cloths, therefore, do not "wear grey."

On the other hand, wool dyeing necessitates extra care and expense in every stage through which it has to pass before leaving the hands of the manufacturer. It must not come in contact with any substance which would injure the colour, or would leave a stain that cannot be removed without inflicting an injury. Hence wool dyeing is more adapted for full dark shades and for permanent colours, than for light shades and fugitive colours. Wool-dyed goods are also less brilliant than such as are piece dyed. The more superficial a colour, the brighter it appears. This arises from the fact that no dye is absolutely opaque, and that the outer surface of a superficially dyed article is lit up by the light reflected from the white fibre below. But if the whole thickness of the tissue is thoroughly dyed, and every fibre saturated with colour, such a reflection of light cannot take place.

Rags and shoddy are dyed in the same manner as loose wool. The chief difference is that the former are not white, like new wool, but retain more or less the colours with which they have been previously dyed, and which it is often impossible entirely to remove. Two general methods prevail in rag dyeing. The rags may either be stripped of their former colour, as far as possible, by the alternate applications of soap-lyes, soda, and dilute acids, and then sorted out to be dyed such colours as they admit;* or the already existing colours may, without stripping, be converted into the desired shades. To give a sample instance of such a conversion, black rags, dyed with logwood and a salt of iron, may be converted into a claret by boiling with so-called "claret spirits," a solution of protochloride of tin. In this operation the tin cuts out the iron, and takes its place in the fibre, thus changing the colour from a black to a claret.

We may here suitably advert to the variable appetite of different samples of wool for colours and mordants. If it is found that a given sample of wool can be dyed to a required shade with a given weight of dye wares, it by no means follows that the same shade can be produced upon another sample with the same quantities. On the contrary, wool from a different breed of sheep, from a different soil or climate, will probably differ in shade, and possibly also in tone.† Hence woollen manufacturers who have a reputation for goods of some particular colour, and who have them dyed on their own premises, are careful to buy year by year the same growths of wool. On the other hand, a public dyer who takes in work from all quarters, finds himself constantly obliged to vary his dye wares in accordance with the changing quality of the wool.

* For instance, an unremoved blue tint in rags would permit them to be dyed purple, violet, or crimson, but would utterly prevent the successful dyeing of an orange, scarlet, ponceau, or even *cerise*.

† The technical use of these words may need explaining. Blue varies *in shade* from one bordering on white to one scarcely distinguishable from black. It varies in *tone* according as it approaches violet on the one hand, or green on the other.

A large quantity of wool is dyed in the state of yarn. Wool and worsted dyed in this state are largely used for knitting and embroidery yarns, for carpets, for table covers, curtains, fancy waistcoatings and dress pieces, shawls, tartans, &c., having a pattern. Similar articles, however, consisting of a mixture of wool or worsted and cotton, and having a pattern of two colours only, can be piece dyed, as will be further explained below.

Yarn dyeing holds a middle place between wool and piece dyeing, the fibre being less readily and thoroughly penetrated than in the former, but more so than in the latter. Great care is requisite that no loose colour, capable of smearing, be left on the yarns. Otherwise the patterns produced by the loom are seriously damaged, the dark shades soiling the adjacent light ones.

The manipulations in woollen-yarn dyeing are simple. The hanks, secured on rods, are immersed in the dye liquids, and turned frequently to secure equal action on all parts of the yarn.

Piece dyeing is a style very extensively, and it may be said increasingly, used for a great variety of woollen cloths and worsted stuffs, such as doeskins, diagonals, merinos, camlets, serges, &c., not to speak of goods with cotton warps. It is generally considered the most economical method of dyeing, other things being equal. The wool can be spun and woven in the most expeditious manner, without any especial arrangements to escape soiling, and the pieces may then be cleaned once for all before being taken to the dye house. The great difficulty in piece dyeing is to insure a perfectly even or level shade over the whole of the piece. If in wool dyeing any small portion should take the colour either more or less readily than the rest, the defect disappears in the subsequent processes, by which the wool is thoroughly mixed up together; but in piece dyeing any part of the surface left darker or lighter than the rest is at once detected. Unevenness of colour may be occasioned by grease or any other kind of dirt, which acts as a resist, and prevents the colour from working on; by particles of aniline colours not thoroughly dissolved, and coming in contact with some portion of the piece; by the use of ill-prepared mordants; by immersing the goods in the dye beck without their being previously perfectly wetted out, or by entering them at too high a temperature, or allowing them to remain too long in one position, &c. Another difficulty, especially in thick goods, is to insure thorough penetration through the whole body of the piece. If this is not effected, and if the dye is deposited on the outer surface alone, it wears off where most exposed to friction. The plant required for piece dyeing consists of pans or becks, capable of being heated to the boiling point, and fitted with rollers, by means of which the pieces can be passed rapidly in and out of the liquid. Facilities for thus winching at a high speed are very requisite, as promoting evenness of shade.

Garment dyeing may be considered as a branch of piece dyeing, from which it differs merely in the fact that the garment dyer, instead of working upon new white materials, operates upon old and worn tissues, upon which he is required to produce either their original colour or a new one. To obtain a level shade under these circumstances is often difficult, and sometimes impossible. For, even supposing that the garment to be re-dyed is perfectly freed from dirt and evenly stripped from the former colour, some parts of it will always be found to have been roughened in the course of wear more than others. Now, wherever such roughening or abrasion has taken place, there the colour will work on more heavily. On the other hand, the garment dyer has one great advantage: he does not ordinarily work to pattern. He is merely required to dye a garment sent him, *e.g.*, a good blue. The manufacturer's dyer, on the other hand, is called on to dye say 100 pieces blue, "as per pattern accompanying." If the result is darker or lighter, brighter or duller, more inclining to the violet or to the green than the pattern sent, he fails in giving satisfaction.

In woollen dyeing a peculiar complication arises from the presence of so-called "burls" or "birls." These are small portions of vegetable substances, bits of straw, down of seeds, and the like, which become entangled in the fleece of the sheep, and are not thoroughly dislodged by all the processes to which wool is submitted. Like all ordinary vegetable matter, their affinity for dyes is, as a rule, feebler than that of wool. They therefore remain colourless, or nearly so, when the cloth comes out of the hands of the dyer, and when numerous give it a spotty appearance. To deal with these blemishes four different methods may be adopted. The burls may be plucked out of the cloth with a kind of tweezers, an operation which if not very carefully performed is apt to damage the surface of the tissue. Or the spots are covered, by means of a blunt pen, with a peculiar preparation known as "burling ink," of which there are different kinds made to suit the colour of the cloth. The pieces are stretched out over a kind of frame in a well-lighted room, and the operation is performed by women known as "burlers." As soon as all the spots on one length of cloth have been covered and rendered invisible a fresh length is drawn on to the frame, till the entire piece has been gone over. Without great care on the part of the burler some of the spots are apt to escape.

A good burling ink should exactly agree in shade and tone with the cloth in question. It must not, when dry, leave a glazed shining spot on the surface, and it must have no action upon the colour of the wool.

Where the burls are very numerous, the whole piece is submitted to an especial dyeing process, adapted to vegetable fibre, being in fact treated as if it were a mixture of wool and cotton. To "burl-dye" black cloths the pieces are steeped in dilute nitrate of iron, and then in a beck of myrobalans or log-wood, or both. In many places an especial quality of nitrate of iron, known as "burling iron," is made for this purpose. Its preparation is a matter of some

nicety. It must contain no hydrochloric acid, or the iron will be deposited upon the wool. It must not contain an excess of free acid, otherwise the dye on the wool may be partially stripped, or at least altered in tone. But on the other hand, it must not be supersaturated or overloaded with iron, or the wool will contract rusty stains which are not easily removed without damage to the dye.

A fourth method of dealing with the burls consists in passing the wool, cleaned but not dyed, through very weak sulphuric acid, and afterwards exposing to a gentle heat. Under these circumstances the vegetable matter is charred and broken up, so as to be subsequently removed by washing without any marked damage to the wool. This method is much more generally employed in France than in England.

Alpaca, vicuna, goat's hair, and all other true animal fibres, are dyed substantially in the same manner as wool.

Silk, for dyeing purposes, is intermediate between wool and the vegetable fibres. Like wool it has a strong affinity for colouring matters, and can be dyed with the bulk of the coal-tar and orchella preparations without the intervention of a mordant. But it is less able than wool to bear the action of strongly acid mordants, and is in most cases dyed at temperatures below the boiling point. Like wool, it cannot be bleached by the action of chlorine and the hypochlorites, such as bleaching-lime, but turns yellow. It is also very readily injured by solutions of alkalies, in which, indeed, it may be readily dissolved. Its affinity for astringents and for iron is very great. By taking advantage of this circumstance the weight of black silks is fraudulently increased to more than 100 per cent. Weighted silks, it must be remembered, are very seriously modified both in their mechanical and their chemical properties. The fibre is deprived of its toughness and elasticity, and becomes brittle. Pure silk is almost incapable of decay under the influences of air and moisture, but weighted silk undergoes a process of eremacausis, or gradual oxidation, and moulders away. Sometimes, when lying in heaps in a warehouse, the absorption of oxygen has been so rapid that a great development of heat ensued, resulting in spontaneous combustion.

The preparation of tin mordants for silks was a matter of great nicety, the sesqui and persalts being preferred. But since the introduction of the coal-tar colours the scope for these preparations may be said to be at an end. For these colours no mordant is ordinarily required in silk dyeing. Indeed, one of the chief difficulties to be overcome in their application to silk was their excessive affinity for the fibre, which caused them to work on unevenly. This evil was overcome, at the suggestion of Mr. Perkins, by mixing the solution of the dye in a weak soap-lye. This moderates the affinity of the colour for the silk, and permits the production of level shades. If the resulting softness of the goods is objected to, they can be rendered hard, or as it is technically called, scroop, by passing it through very weak sulphuric acid, and then rinsing in pure water. All shades of reds, yellows, greens, blues, oranges, violets, as well as lavenders, doves, greys, &c., can now be produced upon silks with the coal-tar colours, as cheaply, and far more beautifully and simply than with the older dye wares.

Silk is dyed in three states—in the hank, in the piece, and as waste and rags. In all these conditions the plant and the manipulations are generally similar to those required in woollen dyeing. That a lower temperature is usual has been already mentioned.

Garment dyeing, or re-dyeing, on account of the high value of the material, plays a still more important part with silk than with wool. To re-dye the weighted silks now so generally sold is rarely practicable. They may be expected to break up on an attempt being made to clean them previously to dyeing.

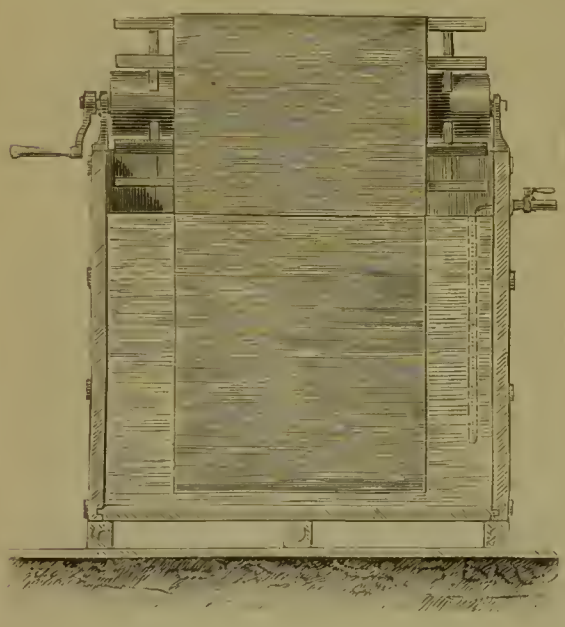
Cotton.—Of the vegetable fibres used in textile manufactures cotton may serve as the type. Its affinities for dyes are much feebler than those of the nitrogenous fibres, wool and silk. Hence, with few exceptions, of which carthamin is perhaps the most important, colours can only be made to combine with it by the intervention of mordants. Even with their aid several colours can only be deposited upon cotton to a slight extent, and in a very loose manner. Vegetable fibre is capable of bearing treatment with alkaline solutions of considerable strength, but it is easily damaged by acids. Hence cotton is generally dyed in neutral solutions. The application of a boiling temperature is rarely found advantageous. It is therefore dyed either cold, or at most at a so-called hand-heat. Cotton has a great affinity for tannin, as occurring in galls, sumach, myrobalans, divi-divi, &c. By being worked in in the extracts of these substances its affinity for many colours is greatly increased. It also combines eagerly with certain metallic oxides or subsalts. It is thus dyed black by successive working in an astringent and in a solution of iron; yellow by being alternately steeped in a solution of lead and in that of a soluble chromate. The mordants for cotton require to be nicely balanced, the base not being held in solution by an excess of any powerful acid. Thus, when alum or sulphate of alumina is employed in cotton dyeing, it is neutralized with carbonate of soda, until a permanent precipitate begins to appear. In this state the alum is enabled to yield up a portion of its alumina to the fibre. Very frequently, however, alumina is used for mordanting cotton in the state of acetate, known technically as red liquor. Acetic acid being much feebler than sulphuric, and being also volatile at common temperatures, parts more readily with its base. The chief compounds of iron used in cotton dyeing are the acetate, known also as black liquor, and the nitrate, more properly called nitro-sulphate. The crude sulphate of iron (copperas) and the chloride have comparatively limited applications. Various preparations of tin are also used in mordanting cottons. They are chiefly sesqui or persalts, and must be neutralized as far as practicable, or, as it is technically called, must be "well killed."

Lead compounds, such as the acetate and nitrate, are also used in cotton dyeing. They have been employed in fixing murexide and certain coal-tar colours upon the vegetable fibre, and more extensively in dyeing chrome yellows.

Lead and tin can also be used in cotton dyeing in alkaline solutions, as the so-called plumbate and stannate of soda. They yield their base to the fibre freely, and may be safely used for mordanting cotton unmixed with wool. If wool be present they are unsafe, as the sulphur which it naturally contains combines with the soda, and reacting upon the metal, causes a black or dark-brown sulphuret to be deposited upon the fibre, and thus stains the goods. Aluminate of soda is also occasionally used with a good effect in cotton dyeing.

Cotton is dyed sometimes as cotton wool, but generally in yarn (hanks), or when woven. The manipulation and the apparatus required are in

Fig. 32.



general similar to those used in woollen dyeing. For cotton pieces, however, and especially for the cotton warps of mixed piece goods, such as delaines, &c., the mordants and colours are now generally applied by the aid of the padding machine. By this the solutions are mechanically pressed into the texture of the piece, and are thus enabled to penetrate the fibre, and combine with it more thoroughly and uniformly than could be effected by mere steeping or wincing in and out of the liquid.

The accompanying sketch, Fig. 32, however, shows an arrangement used in small dyeworks, which is fairly effective.

It must be noted as a distinctive feature in cotton dyeing, that the mordant and the colouring matter are not applied simultaneously, as is often the case in woollen dyeing, but in succession, the mordant first, and the dye afterwards. Were the two placed in the beck together, the general result would be the deposition of the colour not in or upon the fibre to be dyed, but as a lake or precipitate at the bottom of the beck.

Cotton garments, save when mixed with wool or silk, are rarely considered of sufficient value to be redyed. From a similar reason cotton rag dyeing is not a branch of tinctorial industry.

Linen, China grass, jute, hemp, &c., are dyed, when requisite, on the same general principles as cotton.

Mixed Goods.—The warp consisting of cotton or linen, and the weft of silk, wool, or alpaca, are dyed in the piece to an enormous extent. Sometimes it is required to produce in this manner a pattern of two colours, say, for instance, a scarlet design on a yellow ground. If the portions to be coloured consist of wool or worsted, they are dyed scarlet in the ordinary manner, which takes no effect upon the cotton. This is then dyed a gold-yellow with turmeric at a low temperature. In this manner a great variety of two-colour designs can be produced more easily than either by printing or by weaving the pattern with dyed yarns. Shot effects are also easily produced upon mixed goods of this nature. It is probable, however, that before long shot effects of a far superior character will be produced upon tissues of one kind of fibre only, by means of colours having the property of dichroism. Eosin is a dye which may be said to point in this direction, as it imparts to a thread or a woven fabric shades which vary according to the direction in which they are viewed.

In general, however, the object in dyeing pieces of mixed fibre is not to produce figures or shots, but to obtain a uniform colour over the whole surface. As a rule, the wool or worsted is dyed first at a boil, and the cotton afterwards in the cold, or at a hand-heat. Great care is required, and certain processes which would produce the shade required upon either the wool or the cotton singly are not admissible when the two are woven together.

*Dyeing on Wool.*—Indigo is fixed on wool by plunging it in an alkaline solution of indigo white, and then exposing it to contact with the air. The solution is prepared in a vessel usually from 8 to 9 feet in depth, and 6 or 7 feet in diameter, made of wood or copper, and bearing the name of *vat*. These vats are covered with wooden lids, divided into two or three equal segments, and covered over with thick blankets. Without this precaution the bath would be exposed to the atmosphere, and a portion of the indigo would absorb oxygen, and be precipitated.

A most necessary operation, and one of frequent recurrence, consists in agitating the deposit of vegetable and colouring matter formed in the vat, and intimately mixing it in the bath. For this purpose a rake, which is sometimes formed of a strong square piece of wood, set on a long handle, is employed.

Before the tissue is dipped into the dye bath, it is soaked in tepid water, and then hung up and beaten with sticks. In this state it is plunged into the vat, and thus introduces less air into the bath, while the fibre is more uniformly penetrated by the solution. The cloth is now kept in a depth of from 2 to 3 feet

below the surface of the liquid, by means of an open bag or piece of network fixed in the interior of an iron ring, which is suspended by cords, and fixed to the outside of the vat by means of two small iron hooks; the bag is thus drawn backwards and forwards without permitting it to come in contact with the air. When this operation has been continued for a sufficient length of time, the cloth is wrung, and hung up to dry.

Flock wool, when dyed, is inclosed in a fine net, which prevents the least particle from escaping, and which is fixed in the bath in the same way as in the foregoing case.

In England iron vats are chiefly used. These are fixed in brickwork, which extends half way up their surface, whilst a stove is so constructed at this elevation that the flame shall play around their upper part. By this means the vat is heated, and kept at a proper temperature.

The potash vats are usually formed of conical-shaped coppers, surrounded by a suitable furnace. These may be constructed with less depth, inasmuch as there is less precipitation induced in the liquor. By using steam for heating the vats, the employment of copper vessels can be dispensed with, and those of wood adopted.

The vats employed for dyeing wool are known under the names of the pastel vat, the woad vat, the potash vat, the tartar lye vat, and the German vat.

The methods of dyeing by woad or pastel are given by Dumas as follows:—

*Pastel Vat.*—The first care of the dyer, in preparing the vat, should be to furnish the bath with matters capable of combining with the oxygen, whether directly or indirectly, and of giving hydrogen to the indigo. These advantages are found in pastel and woad. Madder is used along with the woad.

The pastel vat ordinarily contains from 18 to 22 lbs. of indigo; 11 lbs of madder might suffice for this proportion, but the large quantity of water which has to be charged with oxidizable matters must be taken into consideration. Even 20 lbs. to a vat of this size have been employed, invariably with the best results. Bran is apt to excite lactic fermentation, and should, therefore, not be employed in too large a quantity; 7 to 9 lbs will be found amply sufficient.

Woad is rich in oxidizable principles, and putrifies with facility. Some dyers use it very freely; but in this bath an equal quantity of it to that of the bran is commonly employed.

In most dye houses the pastel is pounded before introducing it into the vat. The effect of the dye-stuff, when reduced to coarse powder, is more uniform; but this state of division must render its alterations more rapid. When the bath has undergone the necessary ebullition, the pastel should be placed in the vat, the liquor decanted, and at the same time 7 or 8 lbs. of lime added, so as to form an alkaline lye capable of holding the indigo in solution. The whole having been well stirred, it should be allowed to repose for four hours, so that the little pellets may have time to become thoroughly soaked, and thus be prepared for fermentation. Some thick coverings are to be spread over the vessel, so as to prevent contact with the atmosphere. After this lapse of time it is again agitated. The bath at this moment presents no decided character; it has the peculiar odour of the matters which are held in suspension and solution, and has a yellowish-brown hue.

Ordinarily, at the end of twenty-four hours, but sometimes after fifteen or sixteen, the fermentative process is well marked. The odour becomes ammoniacal, while, at the same time, the peculiar smell of pastel is easily perceived. The bath, hitherto of a brown colour, now assumes a decidedly yellowish-red tint. A blue froth, which results from the newly-liberated colour, floats on the liquor as a thick scum. A brilliant pellicle covers the bath; and beneath blue or almost black veins may be distinguished, owing to the indigo of the pastel having an ascendant tendency. If the menstruum be now agitated, the small quantity of indigo which is formed floats on the surface of the bath. On exposing a few drops of this mixture to the air the golden-yellow hue quickly disappears, and is replaced by the blue tint of the indigo. This phenomenon is due to the absorption of the oxygen of the air by the indigo white of the pastel. Wool might be dyed even at this juncture without any further addition of indigo; but colours furnished at this period are devoid of brilliancy and vivacity of tone, while the bath becomes quickly exhausted.

The signs above described announce in a most indubitable manner that fermentation is established, and that the vat has now the power of supplying to the indigo the hydrogen which is required to render it soluble, and this, consequently, is the proper moment for adding the pulverized indigo.

The ordinary guide of the dyer is the odour, which, according to circumstances, becomes more or less ammoniacal. The vat is said to be either *soft* or *harsh*; if the former is the case, it is requisite to add a little more lime. The fresh vat is always soft; it exhales a feeble ammoniacal odour, accompanied with the peculiar smell of pastel, and lime is therefore introduced along with the indigo—from 5 to 6 lbs. are usually employed—and after having stirred the vat, it is carefully covered. The indigo, incapable of solution except by its combination with hydrogen, gives no sign of being dissolved until it has remained a certain time in the bath. It may be remarked that the hard indigoes, as those of Java, require more than six hours for their solution. The vat should be again examined three hours after adding the indigo. The odour is generally by this time weakened; a further quantity of lime is again added, sometimes less, but mostly about equal in amount to the first portion; it is then re-covered, and again left for three hours.

After this lapse of time the vat will be found covered with an abundant froth, and a very evident pellicle of a coppery hue; the veins which float upon its surface are larger and more distinct than they were previously; the liquor becomes of a deep yellowish-

red tinge. On dipping the rake into the bath, and allowing the liquid to run off at the edge, its colour, if viewed against the light, is a well-marked emerald-green, which gradually disappears, in proportion as the indigo absorbs oxygen, and leaves in its place a mere drop, rendered opaque by the blue of the indigo. The smell of the vat is strongly ammoniacal, but the peculiar scent of the pastel is at the same time discernible. When so obvious a character as this is found in the newly-formed vat, the stuff intended to be dyed may fearlessly be plunged in; but the tints given during the first working are never so brilliant as those subsequently obtained. This is owing to the yellow tinctorial matters of the pastel, which, aided by the heat, become fixed on the wool at the same time as the indigo, and thus communicate to it a greenish tint. This accident is common both with the pastel and the woad vats, though it is less marked in the latter.

When the goods have been immersed for about an hour in the vat they should be withdrawn; it would, in fact, be useless to leave them there for a longer time, inasmuch as no more of the colouring principle could be taken up. They are hung up to dry, when the indigo white, by attracting oxygen, becomes insoluble, and acquires the well-known blue colour. If the stuff be now again plunged into the vat, the shade will immediately become deeper, owing to renewed absorption of indigo by the wool. By repeating these operations very deep shades may be communicated.

The pastel in the foregoing mixture may last for several months; but the indigo must be renewed as it becomes exhausted, at the same time adding both bran and madder. In general the following proportions are employed:—

11 to 13 lbs. of good indigo for 100 lbs. of fine wool.

9 to 11 lbs. of good indigo for 100 lbs. of common wool.

9 to 11 lbs. of good indigo for 131 yards of cloth dyed in the piece.

*Woad Vat.*—These vats were extensively employed in the manufactories of the north of France. The bath is prepared in the same manner as for the pastel vat. The finely-cut woad is introduced into the copper along with 2 lbs. of pulverized indigo, 9 lbs. of madder, and 15½ lbs. of slaked lime. The liquor is, after the necessary ebullition, poured upon the woad. This substance contains but a very small quantity of the colouring principle; and some indigo must therefore be added when preparing the vat, so as to indicate the precise instant when the mixture arrives at the point of fermentation requisite for imparting hydrogen to the tinctorial matter, and for rendering it soluble. A large quantity of lime must also be employed, since the woad contains no ammonia resulting from previous decomposition. When the vat is in a suitable state of fermentation, a rusty colour becomes manifest, in addition to the signs already described in speaking of the pastel vat; besides the ammoniacal odour, the bath always retains the peculiar smell of the woad. The pounded indigo is now added, and the operator proceeds in the manner already detailed to reduce it to a state of solution fit for dyeing.

The vats prepared by means of pastel have greater durability than those made with woad; but it is thought that the colours given by the latter are more brilliant than those obtained from the former.

It must be understood that the pastel and woad vats are becoming more and more superseded by the vats to be described below.

The so-called Indian vat was till lately set as follows:—Add 8 lbs. of finely-ground indigo to a bath of water containing bran, 3½ lbs., the same weight of madder, and 12 lbs. of potash. Keep the mixture at 200° Fahr. for some hours, and then cool down to 100° Fahr., when fermentation sets in. In about forty-eight hours the indigo becomes soluble, having been reduced by the decomposition of the saccharine matter, &c., in the madder. The colour of the vat is of a greenish-yellow, more or less covered with a coppery scum.

The use of madder has now been abandoned on account of its expense. The present method is to add to water at 200° Fahr. 20 pails of bran, 26 lbs. of soda crystals, 5 lbs. slaked lime, and 12 lbs. indigo. The temperature is kept up for five hours, and is then allowed to fall to 100° Fahr., when fermentation and solution occur as before. These vats are generally of a conical shape, and are so fixed that a small fire can be maintained around them, or else the temperature is maintained by means of a steam jacket. The Indian vat requires renewing more frequently than the woad and pastel vats, from the indigo being more difficult to dissolve after a certain lapse of time. They should be maintained at a moderate temperature whilst working. They are more easily managed than the woad and pastel vats, the fermentation being much more under control and less liable to change its character.

*Potash Vat.*—This species of vat is extensively employed at Elbeuf for the dyeing of wool in the flock. It presents in all respects a perfect analogy with the Indian vat; in fact, the action of the tartar-lye in the latter preparation depends entirely on the carbonate of potash which it contains. The ingredients used in the preparation of the potash vat are bran, madder, and the potassium carbonate of commerce.

Deep shades are obtained in this species of vat with greater celerity than in all others, a fact which undoubtedly depends on the greater power which potash has of dissolving indigo than is possessed by lime. Experience proves that the potash vat has the advantage in point of celerity of nearly a third; but this is balanced by the inconvenience resulting from the darker shade, which must be attributed to the large quantity of colouring matter of the madder dissolved by the alkaline lye becoming fixed on the stuff with the indigo.

To obtain this vat in its most favourable state, the indigo should be made to undergo a commencement of hydrogenation before turning it into the mixture. For this purpose a bath analogous to that in the vat is prepared in a small copper, to which the pounded

indigo is added. This bath is maintained for twenty-four hours at a moderate heat, taking care to stir it from time to time. The indigo assumes a yellowish colour, dissolves, and in this state is turned into the vat. Many delays and losses are thus avoided in its preparation; and, indeed, it would be desirable if a similar plan were adopted with all these compounds.

*German Vat.*—This vat is of nearly similar dimensions to that used for woad, being three times the size of the potash vat. Its diameter is about 6½ feet, and its depth 8½ feet. Having filled the copper with water, it is to be heated to 200° Fahr.: 20 pailfuls bran, 22 lbs. of carbonate of soda, 11 lbs. of indigo, and 5½ lbs. of lime, thoroughly slaked in powder, are then added. The mixture is well stirred, and left for two hours. The workman should continually watch the progress of the fermentation, moderating it more or less by means of lime or carbonate of soda, so as to get the vat in a working state at the end of twelve, fifteen, or, at the most, eighteen hours. The odour is the only test by which the workman is enabled to judge of the good state of the vat. He must therefore possess considerable tact and experience.

In the process of dipping, 84, 106, or even 130 lbs. of wool are introduced in a net bag, similar to that used in the woad vat, taking care that the bag is not allowed to rest against the sides of the copper. When the wool has sufficiently imbibed the colour the bag containing it is removed, and allowed to drain for a short time over the vessel. In this way two or three quantities are operated upon in succession. The vat is then left for two hours. The workman must be careful to replace the indigo absorbed by the wool, as also to add fresh quantities of bran, lime, and crystallized carbonate of soda, so as to keep the fermentation at a suitable point.

The German vat affords a remarkable saving as compared with the potash vat, but it requires great care and is more difficult to manage. It also economizes labour; one man is amply sufficient for each vat.

*Management of the Vats.*—A good condition of the vat is recognized by the following characters:—The tint of the bath is of a fine golden yellow, and its surface is covered with a bluish froth and a copper-coloured pellicle. On dipping the rake into the bath there escapes bubbles of air, which should burst very slowly; when they vanish quickly it becomes an indication that more lime must be added. The paste at the bottom of the vat, green at the moment of its being drawn up, should become brown in the air; if it remain green, this is a further sign that more lime is required. Lastly, the vat should exhale the odour of indigo. The operator usually completes the assurance of the vat being in a good state by plunging into it, after two hours' respite, a skein of wool, which, on being withdrawn after the lapse of half an hour, should present a green colour, but change directly to blue. The materials of the vat are then once more mixed, and two hours after it may be considered ready for dyeing.

The heat of the vat should never be allowed to fall below 130° Fahr. After each operation the bath must be well stirred and fresh lime added; generally speaking, 1 lb. a day will suffice; the indigo is re-established about every second day. When once this vat is well set, if the operator is careful to examine its working, from two to four batches a day may be dyed with it.

When the stuffs have acquired the desired shade, they are first to be washed in common water, and then in a very weak solution of hydrochloric acid, about 1 part in 1000; after this they are again rinsed in pure water.

When exposed to the influence of putrid fermentation indigo is decomposed and loses its colour. If rendered soluble, it obeys the impulse communicated to the nitrogenized matters with which it is brought into contact, although, if macerated in pure water at the ordinary temperature, it is itself decomposed with great difficulty.

Pastel and woad are very prone to the putrid fermentation, on account of the large quantity of nitrogenous matters which are contained in them; they require, therefore, considerable care in their employment.

When a vat is set, if the fermentation be allowed to continue unchecked, after the appearance of the blue froth and the other signs already indicated, the liquor will acquire a yellow colour similar to that of beer; the froth will become white; it will give out a stale smell and lose its ammoniacal odour; after a few days it will turn whitish, and exhale a smell at first similar to that of putrid animal matter, then it will acquire the smell of rotten eggs, and set free sulphuretted hydrogen. The lime in the pastel and the woad vats, and the tartar-lye and potash in the other mixtures, are used for the purpose of preventing these accidents.

Besides the oxidized compound which is formed by the combination of oxygen with the extractive matters, there is a production of carbonic acid which saturates the alkaline lye, and forms a carbonate of lime in the pastel vat. This is found attached to the sides of the vat in such quantity that the inside of these vessels becomes encrusted with it to a considerable depth. If a piece of woollen tissue be plunged into a vat which has been recently stirred it will acquire a dark colour, and will be found covered with brown stains, which are with difficulty removed. When the woad or pastel vat has been stirred it need be left two or three hours only before plunging in the stuff, at least during the early months of its working, inasmuch as the pastel, being but slightly divided and attenuated, is readily precipitated; but when, by reason of its extreme division in consequence of repeated operations, it is thrown down with less facility, the dipping should not be performed oftener than three times in the day.

The Indian vat requires less time than the others; it may be used an hour after stirring the mixture. The potash being soluble, forms no precipitate; while the fibre of the madder and the pellicles of the

bran become deposited with great facility. One can also dip with these vats much oftener than with those made by pastel or woad.

*Cotton Vat.*—The common blue vat for the dyeing of cotton is made up as follows:—The indigo is first ground in water to an impalpable paste, of the consistence of cream. A quantity of this paste is put into a vessel of water, and a quantity of copperas and slaked lime added, the latter in excess. The whole is well mixed by the rake. When cotton is dipped into this solution, the fibres become filled with white indigo. When lifted out and exposed to the air, the white indigo imbibes oxygen, and becomes converted into blue indigo within the fibre, and constitutes the dye—a beautiful example of chemistry applied to art.

The following vat, based upon a novel principle, has been proposed by Messrs Schützenberger & De Lalande, and has given very satisfactory results upon the large scale:—

A cask, capable of being closed at top so as to exclude the air, is filled with loosely lying feathered zinc, upon which is run a solution of bisulphate of soda at about 30° Beaumé (= spec. grav. 1·26 to 1·30). Here it is allowed to stand for about an hour, and it is better to agitate occasionally by means of suitable machinery. The liquid is then run off into milk of lime, which throws down all the zinc that is in solution. After thoroughly stirring, the whole is allowed to settle, and the clear liquid is drawn off for use. The greatest care must be taken during all these processes to avoid any needless access of air. The clear liquid thus obtained contains hyposulphites of soda and lime. To it is now added finely ground indigo, and enough milk of lime to dissolve the reduced indigo and form a yellow solution, which contains no insoluble matter except what was present as impurities in the indigo. 1 lb. of indigo may thus be dissolved in 4 to 6 quarts of liquid.

For use the vat is filled with water, the solution of indigo is added in quantity, according to the shades required, and the dyeing can be at once begun. Cotton is, as usual, dyed in the cold, and wool and silk at about 80° to 90° Fahr. The vat must be kept slightly alkaline by adding from time to time a little milk of lime. If an addition of lime is needed, the vat looks black instead of a greenish-yellow. If too much lime is present, the wool will be hard, and the indigo will be fixed very loosely upon the fibre. This evil may be corrected by the cautious addition of a little dilute sulphuric acid.

Some practical authorities recommend the following modification of the proportions given above: 100 litres of bisulphite of soda at 5° B., poured into an air-tight stirring cask along with 7 lbs. of zinc powder, and agitated for twenty minutes. Of the clear liquor, 10 litres are taken to 1 kilo. ground indigo, and heated to 60° C.; 1 or 2 litres of milk of lime are added, and if needful a few litres more hydrosulphite till the mixture is a fine yellow.

Leuchs, of Nuremberg, employs as reducing agents in the indigo vat, pectose, pectine, and pectic acid, which may be had in the greatest quantity in turnips. He heats 200 lbs. soda-lye, of spec. grav. 1·35, to 170° Fahr., and adds 2 lbs. of indigo ground to a pulp. In the liquid he then suspends a wire basket containing from 30 to 40 lbs. of sliced turnips, and raises to a boil, air being as far as possible excluded. The cold liquor thus obtained is then mixed with 4 gallons water, and is ready for use: 9 lbs. turnips reduce 1 lb. indigo.

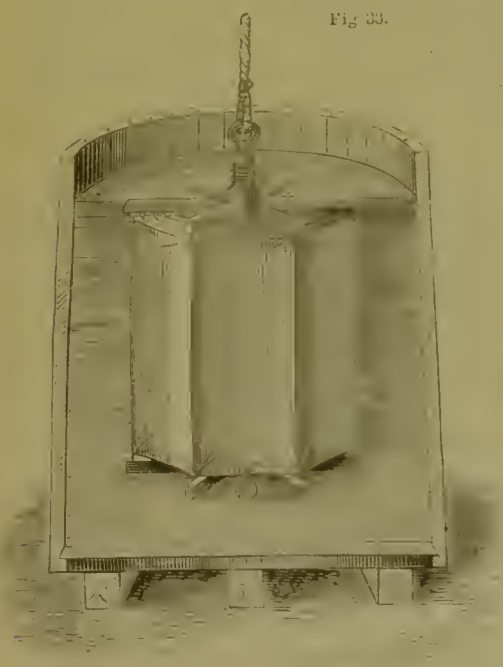
The vats used for dyeing cotton cloth are similar to those used for woollen and silk; but as no heat is required, they are sunk in the ground to a depth convenient for the operators to work at. This size of vat is also used by some for dyeing yarn, but more generally wine pipes or other large casks are employed for this purpose. Five vats constitute a set, and are worked together and kept of the same strength. The yarn being wrought in quantities of 100 lbs., 20 lbs. are passed through each vat. These vats are made up as follows:—Each is filled about three-fourths with cold water, and there is then added 8 lbs. indigo, 16 lb. sulphate of iron (copperas), and 24 lbs. newly-slaked lime. The whole is well stirred with the rake for half an hour, and this is repeated every hour and a half for the first day. The time to stop this agitation is known by the solution becoming of a rich oak-yellow, having large blue veins running through it, and a fine indigo froth on the surface. When these signs are all favourable, the vat is allowed to stand for several hours till all the solid matters settle, when it is ready for use. The reason for employing such deep vessels for vats is to allow room for the collection of the precipitate formed by the sulphate of lime and sesquioxide of iron, which, were they to touch the goods, would deteriorate the colour. The mode of dyeing by this vat consists in simply immersing the goods, and working them in the liquor for fifteen minutes, taking out and wringing or pressing, and then exposing to the air. If the tinge is not sufficiently deep by one immersion or dip, this operation is repeated, but generally in a different vat, and so on until the required depth is obtained. The practice is to begin the dye in the weakest and oldest vats and finish in the newest and strongest, which gives the finest bloom as a finish. All the liquor pressed or wrung out from the goods is put back into the respective vats, and when the operations are finished the vat is raked and allowed to stand till next day. The yarn is well washed in cold water, and then dried. In some cases it is passed through a tub of water acidulated with vitriol till it tastes acid, and then washed, which adds a little brilliancy to the colour when the shade is very deep, and tends to remove some of the iron which may have been fixed upon the fibre.

The quantity of liquid in one of these vats may amount to 100 gallons, so that, by keeping the proportions stated, any quantity of dyeing solution may be made up. Sometimes, from defects in the materials, such as impurities in the indigo, lime, or copperas, or from other causes, the exact appearances stated may not come up satisfactorily: but

a very little practice will enable the operator to vary the process, or add the proper ingredient, so as to produce a good vat. This is a matter, indeed, depending more on experience than on any instructions that can be given. If the indigo is of inferior quality a greater quantity will have to be used. If the sulphate of iron is new and watery, not only more of that substance, but the addition of lime will be necessary; and if the lime is not newly slaked it may not be found very effective, as lime that has stood for some time absorbs carbonic acid, and is thus deteriorated for the vat.

Figs. 33, 34, and 35 depict a very convenient apparatus for dyeing cotton with indigo. The calico is attached by hooks to the frame shown in elevation in Fig. 34 and plan in Fig. 35. This frame is attached to a rope, as in Fig. 33, and by means of a pulley is, when loaded with cloth, dipped into the

Fig 33.



indigo beck. After eight or ten minutes immersion it is withdrawn, and the cloth exposed to the air for a few minutes to blue it, and then again plunged in the dye beck. It is finally washed with much water.

Mineral Dyes and Mordants.—Alum.—Alumina has a strong attraction for organic colouring matters, and hence is used for fixing them upon fabrics: but in order to have the alumina fixed within the fibres of the stuff to be dyed, it must previously be obtained in solution, and this can only be effected by converting the alumina into a salt; hence the dye produced may be, and generally is, not the pure tinctorial matter adhering to the alumina, but in the state in which it is changed and fixed by the salt, the acid element of which acts an important part in altering the tint of the colour. Thus, pure alumina put into a decoction of logwood will become deeply coloured, but the shade of the hue will be different from that obtained by putting into a similar decoction a solution of alum or acetate of alumina. Even the tints obtained by these last two mentioned substances will differ from each other. This is a circumstance which the dyer must ever bear in view, in regulating his tints either by mordants or alterants; and it is this chemical affinity of the colour with the salt of the base that renders it so essential to good results that the mordant, whatever it may be, should be perfectly pure. Alum containing the slightest trace of iron is unsuitable for general use in a dye house.

Fig. 34.

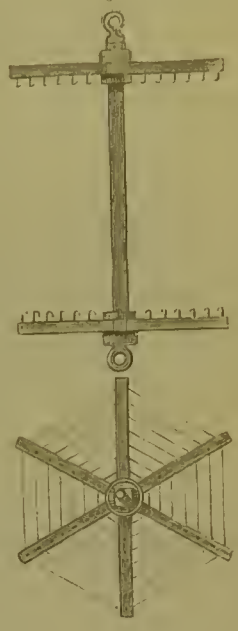


Fig. 35.

Alum is prepared for the dye house by simply dissolving it in water. About 1 lb. of alum to 1 gallon of water makes a good solution. It is not much used as a mordant for cotton, in consequence, doubtless, of the strong attraction which sulphuric acid has for alumina; but it is extensively used in dyeing both silks and woollens, the fibres of which seem to act more powerfully in retaining and fixing the base.

Very nice shades of lavender and lilac may be dyed by making a strong decoction of logwood, and adding to it 1 lb. of alum to 1 lb. of logwood. After standing for a day the cotton is wrought in this solution and wrung out. Light shades are dyed by adding some of this liquor to hot water, working the cotton in it for a time, and then finishing. This preparation is known as the "alum plum tub," or "lavender liquor." It is principally used for light cotton cloth.

Alumina, dissolved in acetic acid, is extensively used as a mordant for cotton in various processes of dyeing, and is known in the trade as "red liquor." The processes for its preparation, and the different results obtained, have already been described under *Acetate of Alumina*, to which the special attention of the dyer is called. The modes of using it will be referred to under the particular processes in which its use is required.

Arsenic.—This metal and its oxides have been already described. Except as a test, it is not very extensively employed in the dye house. The principal use to which it was formerly applied was for dyeing what are technically called "arsenic sages," the colouring principle of which is Scheele's green, dyed by working the cotton through an arsenite of sodium or potassium, and sulphate of copper.

Chromium (atomic weight, 52·2: symbol, Cr.)—This metal was first discovered by Vauquelin in 1797. It derives its name from its compounds being all of a brilliant colour, but as a metal it resembles cast iron in appearance. Hitherto, how-

ever, it has only been obtained in the state of a powder. It is very difficult to fuse, and is not subject to oxidation when exposed to the air. It resists the direct action of common acids—sulphuric, hydrochloric, and nitric. It is found native in considerable quantities in combination with lead and iron. The latter combination, termed chrome iron ore, is its principal source, and is found in America, in different parts of the continent of Europe, and in Scotland. The general composition of the ore is one portion of oxide of iron and one of chromium sesquioxide, or chromic oxide, $Cr_2O_3$.

It is capable of combining with two portions of oxygen, forming—

Sesquioxide, ..... $Cr_2O_3$
Chromium trioxide, ..... $CrO_3$.

The latter oxide in combination with water forms chromic acid, $HCrO_4$. The sesquioxide is a beautiful green-coloured compound, and is generally obtained from the decomposition of the acid by processes about to be described.

The acid is a brilliant scarlet-red coloured compound, and is prepared directly from the chrome ore by crushing the ore very fine, mixing it with a quantity of dried nitrate and carbonate of potassium, and then subjecting the whole to a strong heat in a reverberatory furnace. In this case the nitrate of potassium is decomposed, supplying oxygen to the chromic oxide, which is thus converted into chromium trioxide; and this combines with the alkali, forming chromate of potash, which is afterwards dissolved out by water. This chromate is then converted into the bichromate by the addition of acetic acid, which takes up half of the potassium. The bichromate is next crystallized from its solution, and constitutes the beautiful red-coloured salt so extensively used in dyeing, and known in the trade as "chrome."

The modes of preparing these salts, with the later improvements introduced, will appear under the article Potassium and its Salts. Reference will here be made only to the uses and applications of the bichromate in dyeing. The introduction of this salt into the dye house effected a complete revolution in certain departments of the art, and it still continues to make inroads upon old processes by new and more extensive applications. Its first use was the production of yellow with the salts of lead. By passing the goods through a solution of acetate or nitrate of lead, and then from that through a bath of bichromate of potash, a beautiful yellow is obtained, but some free nitric acid is accumulated in the chrome solution. The same kind of reaction takes place with acetate of lead, and this not only induces a strong tendency to change the shade of colour, but is hurtful to the fibre, while at the same time the process is not economical. These circumstances produced a variety of improvements, which consisted in first converting the lead salt into a subsalt, where two proportions of lead were in combination with one of acid, which met one of the difficulties.

In the dyeing of green, where the cotton was first dyed by the blue vat, as already described, and then dyed yellow, the free acid had a very prejudicial effect upon the indigo; hence it was one of the most difficult dyes to produce of an equal tint. The subsalt of lead did away with this difficulty to a certain extent; but the solution of lead upon the fibre, mixing with the chrome, caused a great precipitation of chromate of lead, producing a rusty colour and a loss of material; and consequently different solutions of lead were used, and also different matters put into the solution of chrome, which, after these remarks, the reader will be able to appreciate by the processes appended to this article for dyeing yellows, &c.

Shortly after the introduction of the chrome yellow dye, the dyeing of orange by the same salts came into practice, and was effected as follows:—A strong deep yellow was dyed upon the cotton: after which it was passed through lime-water brought nearly to the boiling point. This produced chromate of lime and subchromate of lead, which latter possesses a rich orange hue.

The different improvements effected in the dyeing of yellow have been adopted for orange. The object aimed at, with a view to the effective dyeing of this colour, is to obtain a large quantity of chromate of lead fixed upon the goods, so as afterwards to produce a rich orange. The formation of subsalts of lead, by boiling the acetate of lead with litharge, has consequently been largely practised for the dyeing of this colour.

Bichromate of potash is also extensively used, along with catechu, for dyeing browns, fawns drabs, and a great variety of other shades upon cotton. It has of late been much employed in dyeing woollens several shades of browns, blacks, drabs, and slates. With this fabric it acts the part of a mordant, probably by the chromic acid being reduced to the state of chromic oxide ($Cr_2O_3$).

Some dyers reduce the chromic acid into the state of chromic oxide previous to using. The following method has been recommended for effecting this reduction:—Dissolve 9 lbs. of bichromate of potash in 5 gallons of boiling water: then put 10 lbs. of arsenious acid into a boiler containing about 25 gallons of water; boil for a quarter of an hour, and allow the liquor to settle; decant the clear portion into a large vessel while the liquor is still hot, and then add to this clear solution the solution of bichromate of potash, stirring all the time; allow the whole to stand till perfectly cold. It is now put through a filter, upon which is collected the sesquioxide of chromium as a beautiful green-coloured precipitate. This oxide is soluble in hydrochloric acid, and may be used as the dyer finds it convenient, either as a mordant or otherwise. The method of dissolving it in hydrochloric acid is to dilute the acid with water until it no longer gives off fumes; it is then heated, and when hot as much of the sesquioxide of chromium is added as the acid will dissolve; the whole is then left to settle, and the clear portion is decanted. Any free acid

which may still remain is neutralized by adding gradually a solution of carbonate of soda until the chromic oxide begins to be precipitated. The solution thus prepared has a dark-green colour.

This oxide is not much used for cotton, although some beautiful light drabs can be produced by a mixture of this solution with carbonated alkalies; and a variety of shades, varying from blue-black to grey, may be obtained by working cotton in the above-neutralized solution of chromic oxide and then adding a decoction of logwood. The strength of the solution and logwood must be regulated to suit the depth of colour and the particular tint required. The appended receipts will serve to illustrate the use and value of chrome as a dyeing agent, premising that the quantities given are for dyeing 10 lbs. weight of cotton. Of course the operator may either enlarge or reduce the proportions, according to the quantity of goods to be dyed:—

*Light Straw.*—To a tub of cold water add 4 ozs. of acetate of lead, previously dissolved; work the goods through this for fifteen minutes, and wring out; into another tub of water add 2 ozs. bichromate of potash; work the goods through this ten minutes, wring out, and pass again through the lead solution for ten minutes; wash, and dry.

*Lemon Colour.*—Into a tub of cold water put 1 lb. of acetate of lead, previously dissolved; work the goods in this for fifteen minutes, and wring out; into another tub of cold water put 6 ozs. bichromate of potash in solution; work the goods for fifteen minutes through this, and wring out; then put back, and work ten minutes in the lead solution; wring out, wash, and dry.

*Deep Yellow.*—To a tub of cold water add 1 lb. acetate of lead and 1 lb. nitrate of lead in solution; work the goods in this for half an hour, and wring out; then in a tub of warm water add 12 ozs. "chrome," and work the goods from the lead through this for fifteen minutes; expose to the air for half an hour, then pass again through the lead and chrome, working the same time in each as before, and allow an hour's exposure out of the chrome the second time; then pass through the lead; wring out, wash, and dry. If not deep enough, a third dip may be given, observing the same rules.

*Deep Amber Yellow.*—Put into a tub of water 1 lb. acetate of lead, and to this add gradually caustic potash or soda until the precipitate formed be redissolved, taking care not to add more alkali than is required for this solution. The goods are then wrought through this for half an hour; wring out, and then add 8 ozs. chrome in another tub of water, and work the goods in this for fifteen minutes; wring out, wash and dry. 2 or 3 ozs. of sulphate of zinc may be added to the chrome solution with good effect. If a red deep amber be required, add to the chrome solution half a pint of muriatic acid.

*Chrome Green.*—Dye a blue by the vat already described; then, on the top of the blue, dye a yellow, by the last receipt. Of course the depth of blue and yellow will regulate the tint of green, so that the proportions named for the yellow may be smaller, and the dips or immersions repeated more or less frequently, as required. The principal difficulty is when a particular depth or shade of green is wanted, to ascertain the exact shade of blue to be given, as blue cannot be added upon the yellow. This is a matter, indeed, which can only be learned by practice; but a very short experience will suffice.

A few receipts are annexed for dyeing with bichromate of potash upon woollens, the quantities stated being for 5 lbs. of woollen, either in thread, cloth, or wool. It ought to be premised that the woollen must always be well cleaned before dyeing, and that the dyeing must always be performed at a boiling heat:—

*Black.*—Work for an hour in a bath with 8 ozs. bichromate of potash, 6 ozs. alum, 4 ozs. fustic; lift, and expose to the air for a short time; wash well, and then work for an hour in another bath with 4 lbs. logwood, 4 ozs. barwood, 4 ozs. fustic; lift, and add 4 ozs. copperas in solution; work half an hour in this, and then wash and dry.

*Blue-Black* is first dyed blue by vat, or by ferrocyanide of potassium, or *yellow prussiate*, as will be afterwards described, and then proceeded with as directed in the above receipt, only using less materials.

*Fast Lavender.*—The following dye for wool is highly recommended:—For 150 lbs. wool, take 3½ lbs. bichromate of potash and dissolve in sufficient water, in which boil the wool for an hour. In another pan put 8 lbs. logwood and 4 lbs. eudbear loose, and boil them for a few minutes; then enter the wool, and boil for an hour. Finish by adding 1 quart oxalate of tin to 2 gallons water, and add this by degrees, stirring all the time.

*Brown.*—Work for half an hour in 8 ozs. of chrome: lift, and expose till cold; then into a new bath work an hour in 2 lbs. fustic, 4 ozs. madder, 3 ozs. eudbear, 4 ozs. tartar, 2 ozs. logwood; lift out, and dry; or it may be washed before drying.

*Rich Yellow Brown.*—Work for an hour in the following bath:—2 ozs. bichromate of potash, 2 ozs. argol, 2 ozs. alum; wash from this bath; then work for about forty minutes in another bath made up with 2 lbs. fustic, 1 lb. madder, 8 ozs. peachwood, 4 ozs. logwood; wash out of this, and dry. This gives a very beautiful brown; and a great variety of tints and shades may be made by varying the quantities of the last bath with the same preparation as the first bath.

*Rich Yellow.*—Work for half an hour in a bath with 3 ozs. chrome, 2 ozs. alum; lift, and expose till well cooled and drained; then work for another half hour, without previous washing, in another bath with 5 lbs. fustic; wash out, and dry.

*Bottle Green.*—Work for an hour in a bath with 2 ozs. chrome and 4 ozs. alum; lift out, and expose to the air for some time till the goods are cold; then work for an hour in a second bath with 3 lbs. fustic, 1½ lb. logwood; wash out, and dry.

*Invisible Green.*—Work for an hour in a bath with 3 ozs. chrome, 4 ozs. alum; lift, and expose to the air for some time; then work for an hour in a second

bath with 2 lbs. fustic, 3½ lbs. logwood; wash out, and dry.

By comparing these two last receipts it will be seen that the different shades are produced by varying the proportions of the same stuffs.

*Olive.*—Work for an hour in a bath with 4 ozs. chrome, 2 ozs. alum; lift, and expose for some time to the air; then work for an hour in a bath with 3 lbs. fustic, 1½ lb. camwood, 1 lb. logwood; lift out, and dry.

*Purple.*—Work the goods half an hour in a bath with 1 oz. chrome, 1 oz. alum; lift out, and wash in cold water; and then work half an hour in a bath with 2 lbs. logwood, 1 lb. peachwood; lift, and add 1 oz. of alum in solution; work in this for twenty minutes; wash, and dry.

If a light and redder shade be required, use less logwood and more peachwood; and if a darker shade, more of each.

*Rich Green Drab.*—To the dye bath add 1 oz. bichromate of potash, half an oz. alum, half an oz. tartar, and work the goods in this half an hour; lift out, and wash through cold water. Make up a new bath of water, and add 4 ozs. logwood, 2 ozs. fustic, 1 oz. barwood, or half an oz. peachwood; work the goods again through this second bath half an hour; wash, and dry.

Shades of this can also be varied by using different proportions of stuffs.

*Rich Drab.*—Dissolve half an oz. of bichromate, and add the required quantity of water; work in this for half an hour; lift the goods, and add half an oz. of logwood; work again for half an hour; lift out, wash, and dry.

Different shades of this drab may be made by varying the quantities of the dyestuffs.

These receipts might be greatly multiplied; but those which have been given will serve as a guide for practice, and will sufficiently illustrate the extensive use to which bichromate of potash has been applied in dyeing. These directions are also so simple and easy, that even an amateur may put them in practice without risk of failure. The quantity of water to be used is immaterial: this will be regulated according to the size of the vessel, and the number of goods to be dyed; but there should always be enough of water to cover the goods without the necessity of pressing them down. Rules for making up decoctions and other manipulations will be given at the end of this article.

A great variety of effects are produced by the use of the neutral or yellow chromate of potash, of the acetate of chrome, and of chrome alum. The acetate of uranium also produces pleasing grey shades with extracts of madder, commercial and artificial ultramarine.

Copper Salts.—These are not very extensively used in dyeing. They have a peculiar influence in many operations, from their property of yielding oxygen, and thus, for many purposes, they act a very important part, well known to practical men, but not yet easily defined on scientific principles. They are very little used in the dyeing of cotton goods.

Sulphate of copper is used among catechu for destroying the gummy principle in that drug; it is also employed with copperas for certain tints and shades of black and brown upon cottons and woollens.

Iron Salts.—*Copperas.* An important application of sulphate of iron has been already referred to when treating of the common blue vat. The quality of copperas used for this purpose is a highly important consideration. There is a watery-looking pea-green coloured crystal very common in the Scotch market, and which is not a good copperas for the blue vat. When tested, it invariably exhibits a deficiency of iron, and a higher proportion of acid than theory allows; and when such copperas is used for a vat, a greater quantity of it is required, and also more lime. The precipitate in the vat takes a much longer time to subside, producing what is technically termed "swimming," which affects the dye, and is an annoying circumstance to the dyer. The copperas best suited for the blue vat should have a dark rusty-green colour, and care should be taken that it contains no impurities, such as copper, zinc, or alumina, as the presence of these matters neutralizes the effects of iron in reducing the indigo.

The dyer should be acquainted with the means of testing the quality and value of his ingredients. The following are a few simple rules for copperas:—Dissolve 100 grains of the crystals in 4 ozs. of distilled water in a glass or china vessel, add to the solution one quarter oz. of nitric acid, and bring the whole to ebullition; this converts the iron to the state of sesquioxide. Divide the solution into four equal parts. To one part add an excess of caustic potash, and boil for ten minutes; pass the whole through a filter, and fill the filter several times with water to wash the precipitate, which may afterwards be thrown away. To the clear solution add sulphuric or hydrochloric acid until it reddens blue litmus paper; then add ammonia till the solution smells of that liquid, and allow it to stand over for half an hour. If a white precipitate appears, either immediately or after standing, then alumina is present, and the copperas should not be employed for the blue vat.

To another part of the original solution add ammonia in excess, and filter, washing the precipitate as before: but this precipitate is not to be thrown away. If copper be present the solution will have a bluish tint, and the copperas should not be used for the vat; if no blue tint shows itself, and no alumina, dry the filter with the precipitate, and then burn the whole at a red heat for ten minutes, or until the filter is all consumed; sesquioxide of iron remains, and this must be carefully weighed; then, as eighty of this is equal to seventy-two protoxide of iron (ferrous oxide), so will the weight of the residue obtained be equal to the protoxide originally in the copperas; and the quantity of the solution being a fourth of the 100 grains, the result is multiplied by four for the percentage.

The following is the theoretical composition of copperas: —

| | |
|---|---|
| Ferrous oxide, | 25·9 |
| Sulphuric acid, | 28·8 |
| Water, | 45·3 |
| | 100·0 |

So that, if the quantity of ferrous oxide be less than 26 per cent. the copperas is inferior; it ought to be nearer to 27 for good old copperas.

To the third portion of the original solution add a solution of chloride of barium, so long as there is any precipitate formed, and allow it to stand for half an hour; then filter, and wash the filter till a little of the water passing through, caught in a clean glass, gives no precipitate with sulphuric acid; when thus washed the filter with its contents is dried, and then burned in the same way as the iron precipitate; the remainder is weighed, and calculated by this equation:—As 116 sulphate of barium is equal to 40 sulphuric acid, so is the weight obtained to the sulphuric acid present in the copperas; the result multiplied by 4 gives the percentage, which should not exceed 29 per cent., as given above. If, as is often the case, the result be 30 per cent., there is something wrong.

Copperas is extensively used in the dye house for a variety of purposes, from the property it possesses of forming black compounds with vegetable astringent substances, such as gallic acid and tannin; and, as already stated, many of the vegetable dyes contain astringent matters. Iron is consequently of universal use, both as a mordant or base, and as an alterant, and from its sombre effect when used as an alterant it has got the significant epithet of "saddening."

In this salt, as with alumina, although the oxide of iron has a powerful attraction for the vegetable matters, still the acid which is in union with the oxide exercises a strong resistance. Thus, copperas having an excess of acid will not give so deep a dye upon cotton with the same quantity of sumach as dry neutral copperas, nor will either give so deep a tint as the same quantity of ferrous oxide if held in solution by acetic acid. Hence acetate of iron is a more powerful mordant than copperas. Moreover, the reaction of acetic acid upon the other colouring matters that are often present in the vegetable dyes renders that salt of iron much more useful than copperas for many purposes. The latter, however, is most generally used in the dye house. It is much cheaper, and can be applied with greater facility. Solutions of copperas are liable to become slightly changed by attracting oxygen, and the metal being converted into the sesqui. Iron does not in that state suit well for dyeing with astringent matters, as the ferric oxide ($Fe_2O_3$) reacts upon the vegetable dye, and causes loss.

Upon this reaction, and the effect of iron salts upon tannin and gallic acid generally, Grace Calvert made some interesting investigations. The conclusions at which he arrived were these:—1. There can be no doubt that tannic acid is the matter in tanning substances which produces black with iron mordants. 2. That the reason why gallic acid produces no black dye is to be found in the circumstance that it reduces the ferric oxide of iron in the mordant, forming a colourless and soluble gallate of protoxide of iron. 3. That gallic acid has the property of dissolving iron, and thus lays claim to the character of a true acid, whilst tannin, not having this action, appears to be in reality a neutral substance. These observations, some of which had been previously pointed out by Napier, must be of considerable importance to the dyer, and they agree with experience.

Copperas is also used as a mordant for dyeing blue by ferricyanide of potassium. Thus, 10 lbs. of cotton may be dyed a good rich blue by working it for fifteen minutes in a solution of 4 lbs. of copperas, wringing from this, and then working through a solution of 4 ozs. of the ferricyanide; finally, washing in cold water containing an ounce of alum in solution.

Copperas is also used as a dye by the oxidation of the iron within the fibre, thus:—

*Iron Buff or Nankeen.*—Take 2 lbs. of sulphate of iron and dissolve them in warm water, and then add the requisite quantity of water for working the goods; work in this for twenty minutes, and wring out, and put them immediately into a separate vessel filled with lime water, and work in this for fifteen minutes: wring out, and expose to the air for half an hour, when the goods will assume a buff colour. If the colour is not sufficiently deep, this operation may be repeated, working through the same copperas solution, but using fresh lime water each time. The goods are then washed through clean warm water, and dried.

*Chloride of Iron* is another salt seen in the dye house, and is prepared for use thus:—To 4 parts of hydrochloric acid add 2 parts of water, and apply a gentle heat, then add iron in pieces or filings, so long as it continues to be dissolved; then pour off the clear liquid into a basin, and evaporate, when greenish-coloured crystals of chloride will be obtained; but this salt crystallizes with difficulty, and deliquesces in the air, and should not be exposed. Instead of evaporating and crystallizing, the solution may be put into a bottle and reserved for use.

This salt is used for dyeing silks and woollens of a deep blue, and is preferred for that purpose to copperas.

To dye 5 lbs. of silk a rich deep blue, add to water required to work the silk 2 pints of chloride of iron, and 1 pint "double muriate" or chloride of tin; work in this half an hour; lift, and work in a solution of 8 ozs. ferrocyanide. If the colour be now the required depth, wash out in water in which 2 ozs. of alum have been dissolved; but if not sufficiently deep, put it again through the iron and ferricyanide solutions, and then wash out. The preparation of nitrate of iron, so as to suit various purposes, is fully described further on.

*Prussian blues*, and especially the variety known as royal blues upon woollens, are dyed upon a different principle from that followed in the case of cotton. Alternately working the goods in solutions of iron and of prussiate of potash leads to no satisfactory

results. It is therefore necessary to work the wool in a solution of prussiate red or yellow, to which an acid mixture has been added. This decomposes the prussiate, and causes Prussian blue to be deposited upon the fibre. As a specimen of this method we give the following receipt, suitable for producing a fast blue upon 100 lbs. of wool or flannel:—Dissolve 8 lbs. red prussiate, 2 lbs. tartaric acid, 2 lbs. oxalic acid, and the following spirit in water at 208° Fahr., and in it work the goods well for ninety minutes. Lift, drain, rinse, and dry.

For the spirit take 1 lb. of granulated tin, 10 lbs. nitric acid at 36° B., the same weight muriatic acid at 22° B., and 10 lbs. sulphuric acid at 66° B., previously diluted with an equal weight of water.

This is a German process. In England the prussiate is generally decomposed by means of a mixture known as "royal blue spirits." In case of yellow prussiate, the acid mixture used may be sulphuric acid at 90° Tw. 1 gallon, muriatic acid at 32° Tw. half a gallon, and double aqnafortis at 64° Tw. 1 quart. These ingredients should be put together in the open air, and no large stock should be mixed at once. When the red prussiate is intended to be used the nitric acid is quite needless.

The goods are finally bloomed by the addition of some "royal blue finishing spirits," for which purpose an oxalate of tin (see below) is employed.

It must be remembered that, both for silks and woollens, the Prussian blues of every shade are being more and more superseded by aniline blues, and that they will soon have a merely historical interest.

*For Sky Blue.*—The cotton should be previously bleached, then to a tub of cold water, sufficient to work the goods in easily, add half a pint nitrate of iron, and then work in this for twenty minutes; wring out, and pass through one tub of clean water. Into another tub of cold water add 4 ozs. ferrocyanide of potassium in solution, and about a wine-glassful of sulphuric acid; work the goods in this for fifteen minutes; wring out, and wash through cold water in which is dissolved 1 oz. of alum; wring out and dry.

To dye lighter or darker shades of sky-blue use less or more of the iron and ferrocyanide; or should the shade be too light after passing through the processes described, by repeating the operations through the same tubs, only adding an ounce more ferrocyanide, the shade will be deepened nearly double.

*Napoleon Blue.*—The cotton to be bleached before dyeing. Into a tub of cold water add 1 imperial pint of nitrate of iron and 2 gills hydrochloric acid, then add 3 ozs. crystals of tin, or a pint of "double muriate;" stir well, and immediately enter the goods, and work for thirty minutes; wring out, and put directly into the "prussiate tub," made up with water, into which is put a solution of 12 ozs. ferrocyanide and 1 wine-glassful of hydrochloric acid: work in this for fifteen minutes, then wash out in clean water in which is dissolved 2 ozs. alum. If a deeper shade of blue is required than these quantities will give, the goods are washed from the prussiate tub, without alum, in water, and passed again through the iron and ferrocyanide, and then washed out, as above, with alum in last water.

*Royal Blue.*—This is dyed in the same manner as the above; but the liquors are stronger—using 2 pints iron, 2 gills hydrochloric acid, and 4 ozs. tin crystals. The prussiate tub is made up by dissolving in it 1 lb. ferrocyanide of potassium, and adding 1 wine-glassful of sulphuric acid and 1 glassful hydrochloric acid. All the other operations are the same as the preceding. If not sufficiently dark with putting once through, repeat.

For 5 lbs. of silk the following proportions of stuffs are used:—

*Sky Blue.*—To a sufficient quantity of cold water to work the goods add half a pint of nitrate of iron; work in this for twenty minutes, then wash out in cold water.

Into another vessel of cold water add 3 ozs. ferrocyanide of potassium in solution, and 1 oz. by measure of strong sulphuric acid; work through this for ten minutes, then wash in cold water, in which an oz. of alum has been dissolved, and finish.

*Royal Blue.*—Into a vessel with cold water add 2 pints of nitrate of iron; then take 1 pint water and half a pint hydrochloric acid, and to this add 3 ozs. crystals of tin; when dissolved, add this to the vessel containing the iron, or 1 pint double muriate of tin; stir well, and enter the goods immediately, and work for half an hour.

Into another tub dissolve 8 ozs. of the ferrocyanide, and add to it 2 ozs. by measure of sulphuric acid; the goods are wrung out of the iron solution, and put directly into the second vessel with the ferrocyanide, working for fifteen minutes; then wash out in cold water, having 2 ozs. of alum dissolved in it, and finish.

Should the shade not be sufficiently deep, instead of washing in the alum water, they may be put back into the iron solution, and again through the ferrocyanide in the same way, and work the same time as first, only adding 2 ozs. of the latter salt before entering the second time into that vessel; then finish as stated.

Deeper shades are obtained by using more iron and tin, or by giving several dips.

Some wash out the iron solution before going into the ferrocyanide in one water, and also wash it out before putting back into the iron; the shade by this will not be so deep with the same stuff, but there is less risk of an unequal colour.

The finest royal blue on wool and worsted is dyed thus:—for 36 lbs. of goods take 4 lbs. yellow prussiate of potash and 6 lbs. of oxalic acid. Dissolve, and enter the goods at 100° Fahr., and work two hours, raising the temperature gradually to 180° Fahr. Lift and cool. Cool the dye-liquor also with two pails of water; add 21 lbs. alum, and work for half an hour, add three-quarters pint yellow spirits, and work for another hour, raising the temperature gradually to 180° Fahr. again, at which heat work for an hour and a quarter longer.

Lift and add 1 or 2 pints nitrate of iron, according to shade; re-enter the goods, and give five or six turns. Take out, cool, and wash very well. If a very dark shade is required, add a little logwood liquor to the nitrate of iron.

This blue is almost equal in bloom and lustre to aniline blue, but, as will be seen, it is an expensive colour.

It is almost unnecessary to repeat that different quantities will give various depths of colour.

Nankeen or buff colours are dyed directly upon cotton by the nitrate of iron. To a tub of hot water add 1 pint of nitrate of iron, and work in this for half an hour 10 lbs. of cotton previously bleached; wash out in water, and dry. No process could be more simple and easy, and this produces a permanent dye.

These few receipts will show the importance of iron as a dyeing agent. Its further use in the dyeing of blacks, slates, &c., will be given at the close of this article.

*Acetate of Lead.*—See Acetates.

Basic salts of the acetate of lead are prepared for dyeing oranges, and several deep shades of yellow, by boiling a solution of acetate, either white or brown, and adding to it a quantity of litharge, which is taken up, forming salts having two, three, and sometimes six proportions of oxide of lead to one of acid. These are found to be more suitable than the simple acetate. The only use of these lead salts in the dye house is for dyeing yellows, greens, and oranges. They have therefore no application apart from bichromate of potash, which has been already given.

Manganese.—Many years ago the salts of this metal were introduced as a dyeing agent in the production of browns, depending entirely upon the formation of an oxide of the metal within the fibre of the stuff.

The salts of manganese belong to the protoxide; but when the acid which is in union with the oxide is removed the protoxide passes into the peroxide, which has a deep brown colour approaching to black. So that when cotton was steeped or worked for a time in a solution, say, of protosulphate of manganese, and then through a weak solution of an alkali, the acid and alkali combined and were dissolved, while the oxide was left on the cotton. Hence, by exposure to air, it absorbed more oxygen, and passed to a brown; or by passing the cotton through a little bleaching liquor the oxidation of the manganese was immediately effected, and thus brown and fawns of various shades and depths were dyed, according to the strength of the manganese salt, or the number of times the operation was repeated. The colours produced by this means had a heavy dull appearance, and are now very seldom dyed, having been superseded by catechu, which produces similar colours of a lively rich hue.

Prussian Blue.—For the manufacture of red and yellow prussiate see article Potassium Salts. Here the use of these salts in the dye house for the production of Prussian blue will be dwelt upon. The salts of iron have a kind of reciprocal action upon these two salts of potassium, so that with the sesquioxide and yellow prussiate there is produced the same deep blue colour as with the protosalts of iron and red prussiate. This kind of action occurs with several metals, and gives the dyer a considerable power of varying his processes and tints. The following table exhibits these reactions:—

| | Red Prussiate. | Yellow Prussiate. |
|---|---|---|
| Protosalts of manganese, | Brown, | White, becoming red. |
| Lead, | No precipitate, | White. |
| Ferric salts, | No precipitate, | Deep blue. |
| Ferrous salts, | Deep blue, | Bluish-white. |
| Copper, | Yellow-green, | Brown. |
| Stannous salts, / Stannic salts, | White, | White. |
| Persalts of tin, | No precipitate, | Yellow. |
| Zinc, | Orange-yellow, | White. |
| Bismuth, | Yellow, | White. |
| Cadmium, | Yellow, | White. |
| Cobalt, | Red-brown, | Green. |
| Nickel, | Yellow-green, | Greenish-white. |

These two salts—yellow and red prussiate, *i.e.*, ferro- and ferri-cyanide of potassium—are of the utmost value to the dyer. From the above table it will be seen that different colours may be produced by using different metallic salts; as, for example, copper and ferrocyanide of potassium. By working the goods in a solution of sulphate of copper, and then passing them through a yellow solution of yellow prussiate, a rich brown is produced of great permanency, and this method is occasionally practised.

The principal use of these prussiate salts, however, is in dyeing blues by the salts of iron, examples of which have been given just above; other instances will also be appended, but in order to explain the nature of the process by which the colour is produced, the yellow prussiate may be defined as a double salt of iron and potassium, combined with cyanogen, namely, one part cyanide of iron and two parts cyanide of potassium.

The mere introduction of oxide of iron into a solution of yellow prussiate will not convert the iron into Prussian blue; and therefore, if a piece of calico, having its fibres saturated with oxide of iron, were passed through a solution of pure ferrocyanide of potassium, there would be no blue dye obtained, as the potassium would retain the cyanogen, and prevent it combining with the iron. The presence of an acid is requisite to unite with the alkali metal, thus setting the cyanogen free. When the goods are dyed by lifting them out of the iron solution, and putting them directly into the solution of yellow prussiate, in that case the acid of the iron seizes the potassium, and a mutual transference ensues.

When the cloth is charged with the iron salt, and the acid is removed either by washing or passing through an alkali, as is often done, in that case acid must be added to the prussiate solution to liberate the cyanogen. If care is not taken in practising this process, a certain loss will occur. When the acid is added to the prussiate solution, a great quantity of the cyanogen passes off as hydrocyanic acid, and forms a new compound of iron and the liberated cyanogen. This, indeed, is also a species of Prussian

blue, but the product is far short in colour of what would be obtained if no acid had been added. These observations will guide the intelligent dyer in his mode of proceeding with this agent. The same remarks apply also to red prussiate in its practical application. Colours dyed by the prussiate should be dried by the air alone; for heat and moisture have a strong action on Prussian blue, producing first a reddish tint, which passes into lavender and then into grey, and if the action is continued, the tint is completely destroyed. It is easily affected also by the sun's rays, and likewise by washing in distilled or rain water. All alkaline matters destroy it. In the deeper shades of Prussian blue, where tin salts are used along with the iron, the colour is much more permanent. All kinds of fabrics —cotton, silk, and woollen—admit of being dyed Prussian blue.

TARTAR.—*Argol—Cream of Tartar—Bitartrate of Potash.*—This salt is much used as an adjunct in the dyeing of woollen stuffs. It is seldom employed alone, but mostly with alum, sulphate of iron, and chloride of tin. Its use, along with these bodies, is very important, owing, as is generally supposed, to a decomposition taking place, in which the sulphuric acid of the alum and iron, and the chlorine of the tin, unite with the potash of the tartar, resulting in the formation of a tartrate of alumina, iron, or tin, which combines more easily with the woollen stuff. With reference to this action DUMAS has the following:—

"Cream of tartar, or bitartrate of potash, constitutes by itself a very feeble mordant, but which is often used in dyeing light woollen stuffs, to which one may wish to give a delicate but brilliant shade. It is also employed in the dyeing of ordinary woollen goods, but here it is associated with alum, sulphate of iron, chloride of tin, &c. Its influence under these circumstances consists evidently in determining a double decomposition, from which a sulphate of potash or chloride of potassium is produced, whilst the tartaric acid combines with the alumina, the sesquioxide of iron, or the oxide of tin. Now, it is very probable that the colouring matters remove the alumina, the sesquioxide of iron, or the oxide of tin, more readily from tartaric than from sulphuric acid. Moreover, the presence of free sulphuric acid would certainly prove injurious, as well to the stuff as to the colouring matter, whilst free tartaric acid can exercise no unfavourable action over them."

The operation of subjecting wool to the alum mordant is always effected at the boiling point; the mixture used in this process is a compound of alum and of cream of tartar. One of the objects of this addition is to free the bath of the carbonate of lime which the water generally retains in solution, and which, acting on the alum, would determine its partial decomposition by producing an insoluble aluminous sulphate of aluminium and potassium, and this accumulating on the stuff, and becoming unequally fixed upon its surface, would lead to stains or blotches on passing the material through the dye bath. But, independently of the above effect, which might be produced by any acid, cream of tartar appears to be capable of effecting a further object, by inducing a double decomposition, which transforms the alum into a tartrate of aluminium. However this may be, after one or two hours boiling in the alum bath, the cloth, which should be constantly agitated so as to cause a more equal application of the mordant, is withdrawn from the copper, and after thoroughly draining, it should be put aside for two or three days, when it is wished to dye it with any full-bodied colour. Experience has proved that this repose after the use of the mordant greatly favours the union of the latter with the stuff. In applying the tin mordants, use is also made of cream of tartar. It is, moreover, an indispensable addition where it is desired to fix the salts of iron previously to dyeing in black.

Woollen cloth on being dipped into a cold aqueous solution of alum appropriates to itself a part of this salt, but without undergoing any very sensible alteration. MM. THÉNARD and ROARD have, indeed, proved that cloth, when thus treated by a cold solution of alum, gives up this salt to boiling water, and that after a few washings performed at the boiling point it will have parted with the whole of the alum which it had received in the cold bath. When, however, cloth is boiled in a solution of alum, it yields to this liquid a portion of its organic matter, which becomes dissolved; but, at the same time, it absorbs an equal amount of the alum.

It will now merely be necessary to show the action which wool undergoes when brought into contact with alum and cream of tartar at one and the same time. It is very possible that there may be in this case a simultaneous fixing of alum, as well as of the double tartrate of aluminium and potassium, and of tartaric acid. The presence of alum in the cloth when taken from the boiling solution is very evident; that of tartrate of aluminium and potassium and of free tartaric acid is only presumable.

Tartar is often adulterated when sold to the dyer. Its adulterations are generally sand, carbonate of lime, alum, and sulphate of potassium. By boiling 100 grains of the tartar in a solution of carbonate of potash or borax, the sand, if any be present, will remain as an insoluble residue, and may be weighed.

Take another 100 grains of the same, finely ground, to which add a little water, and then a little dilute hydrochloric acid; if chalk be present, there will be effervescence. After allowing it to stand for half an hour, add ammonia till the solution smells of that alkali; then put the whole upon a filter, and wash. To the clear filtrate add a solution of ammonium oxalate, which will precipitate the lime; this, when filtered and burned, gives the quantity of carbonate of lime in the sample.

Dissolve another portion in water, with a little hydrochloric acid, and filter; to a part of the filtrate add a few drops of chloride of barium; if a white precipitate is formed, sulphuric acid is present. To the other portion of the filtrate add ammonia; if no precipitate is formed by this, then the adulterant will be sulphate or bisulphate of potassium; but

should there be a white gelatinous precipitate by ammonia, alum is present in the tartar. The latter salt is not injurious to the process to which the tartar is applied by the dyer; but it is well that he should know the quality of the stuff before using it.

Tin.—The oxides of this metal have been long known as a mordant for dyeing, as stated in the course of the historical remarks; and the salts of tin are still among the most useful and extensively used of any substances in the art. The oxides have a strong affinity for vegetable colouring matters, and also a strong tendency to combine with or become insoluble within the fibres of the goods submitted to their action, thus rendering them peculiarly suitable as mordants. Tin combines with oxygen in different proportions, while its oxides combine with acids, and give rise to a series of salts of distinctive qualities, but all more or less useful in dyeing. These oxides have the following composition :—

| | |
|---|---|
| Monoxide or stannous oxide, | $SnO$ |
| Sesquioxide, | $Sn_2O_3$ |
| Dioxide or stannic oxide, | $SnO_2$ |

The first and last of these form with acids permanent salts, which are distinguished as stannous and stannic salts. The sesquioxide salts are used in dyeing under the name of "bowl spirits" or "nitrate of tin."

*Hydrated stannous chloride, tin salt*, $SnCl_2,2H_2O$, is obtained in the market in the form of white prismatic crystals, which, according to Penny, contain two equivalents of water, and are therefore composed of—

| | |
|---|---|
| Tin, | 52 |
| Chlorine, | 32 |
| Water, | 16 |
| | 100 |

Other chemists, however, have assigned three atoms of water, in which case the composition will be—

| | |
|---|---|
| Tin, | 48·1 |
| Chlorine, | 29·5 |
| Water, | 22·4 |
| | 100·0 |

The quantity of tin found in the salts of commerce generally agrees better with the latter analysis than the former. When these salts are put into water they produce a milky-coloured solution, owing to the formation of an oxychloride of tin, which is insoluble. A little hydrochloric acid put into the water prevents this to a large extent.

Besides these crystals of tin, there are also obtained in the market solutions of dichloride of tin, under the name of "single" and "double muriate." The former is a solution of tin in hydrochloric acid, with excess of acid, and the whole diluted with water. The quantity of tin in good single muriate is 12 per cent.—$SnCl_2$ (stannous chloride).

*Double muriate* is a strong solution of the protochloride, $SnCl_2$; it contains about 25 per cent. of tin. Both these salts vary very much in quality, and should always be subjected to a testing process. That recommended by Penny is very easy and simple, and also very correct in its results.

Dichloride of tin is extensively employed by dyers and printers under the names of crystals, or salt of tin, and single and double muriate of tin; the first is the salt in its crystallized state, and the others are solutions of it in water, with excess of hydrochloric acid. The consumption of these articles is very considerable. In Glasgow alone the production of crystals of tin, in the course of a year, is estimated at from 150 to 200 tons; and in Manchester and its neighbourhood the annual consumption is even greater than this, being perhaps not less than from 250 to 300 tons.

The principal adventitious matters contained in the crystallized chloride are water and excess of hydrochloric acid, arising from imperfect drainage of the crystals. This is particularly the case with fibrous or feathery crystals, which have the power of retaining mechanically a considerable proportion of the mother liquor.

The value of tin salts, as respects the several purposes to which they are applied in dyeing, depends evidently on the amount of tin they contain; it being also essential that the metal should exist exclusively in the state of stannous chloride.

The agent which Penny was the first to propose to employ is bichromate of potash. Its application is based upon the fact that chromic acid, in presence of free hydrochloric acid, converts dichloride of tin into tetrachloride, the chromic acid becoming sesquichloride of chromium. The details of the process will be found below.

*Sesquichloride of tin* (stannous - stannic chloride, $Sn_4Cl_6$) may be prepared by putting into a solution of dichloride of tin a quantity of newly precipitated sesquioxide of iron, when a double decomposition takes place. Two parts of dichloride of tin and 1 part of the sesquioxide give 2 of monochloride of iron and 1 of sesquioxide of tin.

This sesquioxide of tin is precipitated, collected, washed free of iron, and then redissolved in hydrochloric acid, forming a stannous-stannic compound of chlorine. This salt has several distinctive properties in its reaction with other bodies; and in many practical operations in dyeing it is more than probable that this class of salts plays an important part. It will be seen, under the head Iron in this article, that some of the blues there mentioned are, in all probability, dependent upon the formation of this salt for their peculiar tint.

Stannic salts are produced by the solution of the dioxide in an acid. The principal acid salt of this sort used in the dye-house is the dichloride. When tin is dissolved in hydrochloric acid, with nitric acid present, and the temperature is allowed to rise, a tetrachloride will be formed. Dyers, in dissolving for mordants, generally use a mixture of hydrochloric and nitric acids. If care be taken to keep the solution cool a dichloride is formed, notwithstanding the presence of nitric acid; but should tin be added in too great quantity at a time, the heat will be so much increased by the rapid action that a

tetrachloride will be the result; and there is often produced, in the preparation of these salts, a mixture of monosalts, sesquisalts, and disalts. Hence the cause of the irregularity of tint produced by tin mordants thus prepared; very great care must therefore be taken in the preparation of such salts.

Tetrachloride, $SnCl_4$, is often desirable as a mordant, and in that case it may be prepared by dissolving some crystals of the salts of tin, or a quantity of single or double muriate, and passing through the solution a current of chlorine gas (see Chlorine), or by heating the solution, and adding to it when hot some nitric acid. Care must be taken in this last process not to add the acid in too great quantity at a time, as violent effervescence ensues, and the contents will boil over, causing loss. The technical name of the tetrachloride of tin or stannic chloride is "oxychloride."

The acid preparations of tin used in dyeing are called "spirits," with a term prefixed to each, denoting their particular application, as red spirits, barwood spirits, plum spirits, &c. Their preparation is performed by melting the tin in an iron pot and pouring the metal from some height into a vessel filled with cold water, which granulates the tin into lamellar masses. This process is termed "feathering" the tin.

*Acetates* and *oxalates of tin* are also used occasionally for dyeing purposes by adding a solution of acetate of sodium or potassium to chloride of tin for the acetate, and a solution of oxalate of soda or potassa for the oxalate of tin. In both cases a double decomposition takes place, the chlorine combining with the alkali and the acid with the tin. The reactions and the precipitates of the acid salts of tin, with other reagents, are as follow:—

| | Monosalts. | Disalts. |
|---|---|---|
| Potash and soda, | White, soluble in excess, | White, soluble in excess. |
| Ammonia, | White, insoluble in excess, | White, soluble in excess. |
| Carbonate of the alkalies, | White, soluble in caustic alkalies, | White, soluble in caustic alkalies. |
| Yellow prussiate, | White, | None. |
| Red prussiate, | White, | None. |
| Galls, | Slight yellow, | None. |
| Gold, | Deep purple, | None. |
| Sulphides of the alkalies, | Brown, | Yellow, soluble in caustic potassa. |

Besides the acid salts of tin there is a series of alkaline salts, in which the stannic oxide combines with alkalies in the same manner as an acid, and forms definite compounds, named stannates. The stannate of soda has been of late years extensively used as a dyeing agent. The mode of its preparation has been the subject of several patents. The general method is to fuse the oxide of tin with soda, either caustic or carbonate, at a red heat, then dissolving the fused mass in water, and crystallizing. When metallic tin is used instead of oxide, a quantity of nitrate of potassa is put in with the alkali, which by decomposition converts the tin into an oxide. The following extracts from the specification of James Young's patent will give a general idea of the methods by which such salts are to be prepared, including stannates and stannites of the alkalies:—

Firstly. To make stannate of soda, he puts a quantity of tin ore, or what is commonly known in Cornwall by the name of *black tin*, reduced to powder, into an iron pot, along with a solution of caustic soda, and sets the pot on a fire to boil. The proportions in which he uses these ingredients vary with their respective qualities. If the ore contain 70 per cent. of tin, he employs about two and a half times its weight of caustic soda liquor, containing about 22 per cent. of soda, increasing or diminishing the proportion of the liquor employed according as it is desired to produce a stannate with a greater or less excess of alkali. The materials are kept well stirred and the heat gradually raised up to between 500° and 600° Fahr., at which temperature the ore is acted upon by the soda, and the tin or oxide of tin contained therein, or the greater part thereof, combines with the alkali. The progress of the operation may be known from time to time by taking out of the pot a small portion of the mass, and ascertaining how much of it dissolves in water, and how much of the ore has been left unacted upon. The hot mass is then transferred from the pot to another vessel, and set to cool. And when cooled it is mixed with water, when any insoluble matters which may have remained in it, unaffected by the caustic soda, are easily separated by filtration or by subsidence. The clear liquor which remains is the stannate required, which may be either employed in that state or evaporated to dryness, or crystallized, the solid salt being dissolved as required for use.

Secondly. This chemist also prepares stannate of soda by mixing a quantity of tin ore, reduced to powder, with one and a half times its weight of nitrate of soda, subjecting the mixture to a red heat in an iron vessel, passing a current of steam over it, and keeping it constantly stirred during the operation, in order to expose fresh portions of it to the action of the steam. Nitric and nitrous acids are given off in fumes, which may be condensed with water, and collected as collateral products—reducing thereby the cost of the stannate. Stannate remains, which may be freed from its insoluble impurities by mixing it with water, and filtration or subsidence, as in the process first before described; and it may be also left either in a state of solution, or crystallized or evaporated, as aforesaid.

Thirdly. He substitutes for the nitrate of soda employed in the last preceding process chloride of sodium—common salt—using, however, equal weights of the salt and tin ore; and pursuing the same method in all other respects, he also obtains thereby stannate of soda, with hydrochloric acid as the collateral product.

Fourthly. He procures by the following process both stannite of soda and stannate of soda. He subjects to a red heat a quantity of metallic tin,

mixed with an equal weight of solid hydrate of caustic soda (which may be obtained by boiling down caustic soda liquor, say 3½ cwts. of the liquor containing 22 per cent. of soda to about 1 cwt. of the hydrate), stirring the materials well during the operation; whereupon the water of the sodium hydrate becomes decomposed, and parts with its oxygen to the tin, and the stannous oxide so formed, uniting with the soda, forms a stannite of soda, suitable for some dyeing and printing purposes. To convert this stannite of soda into a stannate of soda, it is boiled in water, on which a portion of metallic tin is precipitated in the form of a black powder, and the solution remaining is stannate of soda. Or, 20 parts of metallic tin are taken, 16 parts of solid hydrate of caustic soda, and 3 parts of oxide of manganese, all by weight, and subjected to a red heat in an open pot, keeping the mixture constantly agitated, and allowing a free access of air. So small a portion of oxide of manganese as is contained in this mixture would be quite insufficient of itself to further oxidize all the tin, but this oxide of manganese is converted by the heat and absorption of oxygen from the atmosphere into a manganate of sodium, which salt becomes decomposed by the tin, and part of it goes to form dioxide of tin, leaving a residuum of oxide of manganese; this becomes once more, by a new absorption of atmospheric oxygen, a manganate, which is decomposed by the tin as before, yielding a fresh accession of binoxide of tin; and so the process goes on until all, or nearly all, the tin has become stannic acid and combined with the soda. The mass in the pot is then dissolved in water, and the solution clarified by filtration or subsidence. The supernatant liquid is a solution of stannate of soda, which may be either left as it is, or crystallized, or evaporated to dryness, as aforesaid. The precipitated oxide of manganese may be collected and used over again for the same purpose.

The stannite formed in the first of the processes described under this branch of Young's specification, may be changed into stannate of soda by merely keeping it freely exposed at a red heat to the atmosphere for a sufficient length of time; but preference is given to manganese as the oxidizing agent, being more expeditious, and, on the whole, cheaper.

Fifthly. He also employs for the formation of stannate of soda, oxide of tin, which is obtained by heating metallic tin to redness in an iron vessel, keeping it well stirred, and passing a current of steam or air over it. And this oxide of tin is treated, along with caustic soda, in precisely the same way as the ore has been before directed to be managed.

Sixthly. Stannate of potash is manufactured by each and every of the methods before described of manufacturing stannate of soda, substituting only in each case where caustic soda, or nitrate of soda, or chloride of sodium is directed to be employed, an equivalent of caustic potash, or of nitrate of potash, or of the chloride of potassium, as the case may be.

Seventhly. This chemist also manufactures stannite of potash by the same process as stannite of soda is before directed to be produced, substituting for the hydrate of soda an equivalent of hydrate of potash.

Another preparation of tin with alkalies has been introduced into dyeing operations—a double salt of soda with arsenic and stannic acids, termed arseno-stannate or arseno-stannite of soda. Unless applied to some purpose for which no substitute could be used with anything like the same advantage, the use of these deadly poisons should be avoided. At all events, a higher motive should exist than mere economy in producing a certain tint upon a dyed or printed article.

Stannate of soda is used as a mordant in print and dye works. Numerous experiments have been made with it on a large scale, to decide whether, in calico printing or dyeing, the hydrated dioxide of tin alone would be preferable to an arseniate of the same oxide as a mordant. The result of comparative trials leads to the preference of hydrated stannic oxide alone, the various shades being more brilliant and less liable to unevenness than when arsenic acid is present. It would be desirable to substitute in commerce a purer stannate of soda for that at present sold, as well as for that containing arseniate of soda.

Zinc.—The only salt of this metal used in the dye house is the sulphate—white copperas or white vitriol—and even this is not used to any great extent, nor for the direct purpose of a dye or mordant, but for certain qualities which the oxide possesses in reacting upon other mordants; and as the precipitate with zinc salts are mostly all white, the sulphate is occasionally used to modify the action of stronger agents, by a double decomposition, where the oxide formed does not affect the tint, as in bichromate of potash in dyeing yellows. Further, as it parts with a portion of its oxygen when in contact with de-oxidizing agents, it is made to serve a purpose in some of the processes in calico printing.

Organic Colouring Matters.—The majority of these are sufficiently described in the introduction to this article; it is only needful here to give a few manipulative details respecting the most important of them.

Archil *or Orchil.*—*Orseille*, French; *Persio*, German.—A violet-coloured paste prepared from different species of lichens, particularly *Roccella tinctoria*, *R. corallina*.

*Orchil* may be regarded as the English, *cudbear* as the Scotch, and *litmus* as the Dutch name for one and the same substance; the first being generally fabricated in the form of a liquid of a beautiful reddish or purple hue, the second chiefly in that of a powder of a lake or red colour, while the third is in that of small blue parallelopipeds or cakes. The latter variety differs in the greatest degree from the others in colour and consistence; its tinge is imparted by the addition of an alkaline carbonate, and sometimes, as an adulteration, of indigo; and its consistence by the presence of thickening agents, such as gypsum, starch, chalk, or various silicious and argillaceous matters.

Archil, cudbear, and litmus are now manufactured

in England, either from the same species of dye-lichen, or from a variety of kinds, by altering the process of manufacture.

The lichens, which are principally collected on rocks adjacent to the sea, are cleaned and ground into a pulp with water; ammoniacal liquors are from time to time added, and the mass is frequently agitated, to expose it as much as possible to the action of the atmosphere. The colouring matter is thus expressed. Chalk, plaster of Paris, or other substance, is sometimes added to it to increase its consistency.

In the most recent process the lichens, previously sorted and washed several times with cold water, are ground up to a somewhat liquid paste. This paste is exhausted by washing several times with cold water. The liquids obtained are filtered through a peculiar kind of loosely-woven, felty, woollen tissue, which retains the ligneous matter, but admits of the passage of the partly dissolved, partly suspended colorable acids. By the addition of a small quantity of bichloride of tin the colouring matters are coagulated and collected on filters made of stout linen tissue. After having been once more washed with water the mass is dissolved in ammonia, and placed in properly-constructed tanks, wherein, by the aid of a suitable temperature and frequent stirring, the material is converted into orchil. The operation is one which occupies a long time. Its progress is tested by dyeing, with a certain weight of the orchil, a certain size of woollen tissue.

*Archil Paste.*—The ordinary method of preparing archil paste is as follows:—The apparatus used is a wrought-iron horizontal cylinder, made very smooth within, about 6 feet in length and 3 feet in diameter. The lowest third part of the circumference for the entire length is fitted with a steam jacket for the application of heat. A shaft runs through the cylinder axially from end to end, with a movable lid for introducing the charge of weed and ammonia. There are also a few small slides for regulating the supply of air.

A cylinder of the dimensions given is charged with 100 lbs. of weed and 540 lbs. of ammonia at 5° of the common ammonia glass, which corresponds almost exactly with Beaumé's hydrometer for liquids lighter than water. The charge can be ready in three days, but the quality is improved if worked for a week. Steam is admitted into the casing by a pipe at the end opposite the man-hole, and the temperature is kept up to such a height that the paste feels slightly uncomfortable to the hand—about 140° Fahr. (60° C.). The agitator is kept gently revolving during the whole time.

The yield for the quantity above given is 540 lbs., or three times the weight of the weed employed.

An excess of ammonia renders the colour less stable, impairing its affinity for the fibre. It should be mentioned that the blue shade makes its appearance first, and by proper management the change can, if desired, be arrested at this point. The red shade appears when the joint action of air and ammonia is allowed to proceed to a greater length.

*Archil Liquor.*—The weeds are boiled out with water and strained; the extract is concentrated to 8° to 10° Tw., and then reheated and agitated with ammonia at 24° of the ammonia glass. Continual agitation is here not necessary.

The arrangements for extracting the weeds are various. It is generally boiled in three successive waters, the first and second liquors being mixed and concentrated, whilst the third serves for the first extraction of a fresh quantity of the woad.

The weeds for paste and liquor should not be ground too fine, but should be bruised under edge-stones rather than pulverized. Certain additions are frequently made by manufacturers.

Small quantities of red prussiate (potassium ferricyanide) gives the archil a redder tone, whilst a slight addition of a fixed alkali (generally carbonate of potash) gives an extra blue shade. A little tartar or white argol improves the bloom and brilliancy.

*Cudbear.*—Archil paste, made as above described, is dried at a steam-heat, and afterwards ground to a fine powder in a lac-mill. It is very generally weighted with common salt, and its appearance is often factitiously improved by the addition of a little magenta.

Archil is sometimes fraudulently mixed with extracts of logwood, sapan, &c.

When the amount of logwood extract in archil is considerable, it will be indicated, on the addition of alum or protochloride of tin, by the shade produced, as compared with pure orchil treated in the same manner. These reactions, however, are not decisive, and are of value only when taken together with others.

When about 50 drops of pure archil, diluted with 3 ozs. of water, and slightly acidified by means of acetic acid, are mixed with 50 drops of fresh solution of protochloride of tin—1 part of the salt in 2 of water—and heated in a flask upon a sand-bath, the colour is almost entirely destroyed when the liquid is at the boiling point, presenting only a yellowish tinge.

A drop of logwood extract, diluted with 3 ozs. of water, and treated in the same manner, produces a distinct violet, which remains unaltered after several hours' boiling.

The violet colour produced by logwood extract is capable of indicating the presence of logwood, even when it does not amount to more than 3 or 4 per cent. of the orchil. The boiled liquid has then a permanent grey tint.

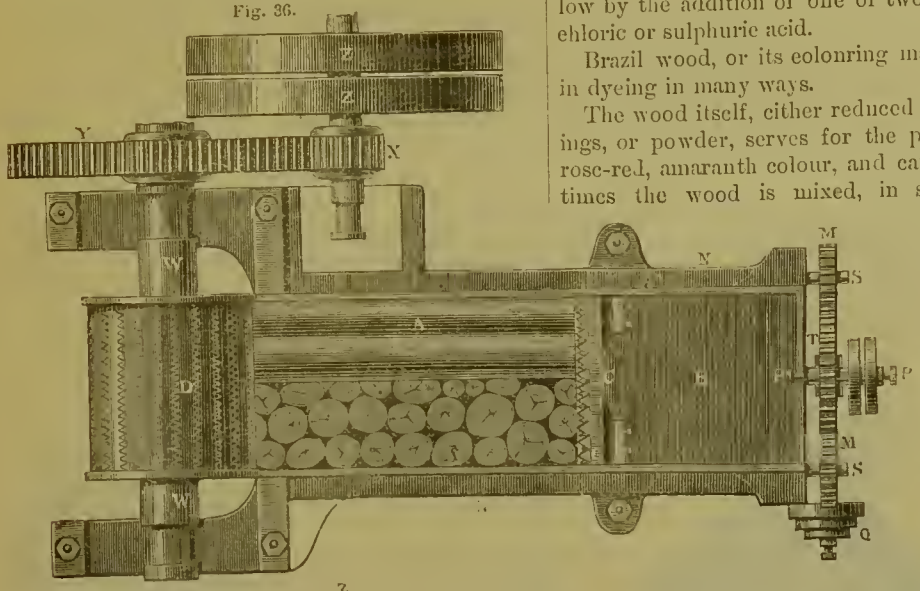
When the adulterating substance is extract of lima or sapan wood, the boiled liquid retains a red hue.

Blue archil, when mixed with a small quantity of ferrocyanide of potassium, acquires all the properties of the red. The presence of the ferrocyanide does not interfere with the above method of testing for wood extracts.

Archil and cudbear are extensively used in dyeing woollen for a great many colours, as purple, lavender, lilacs, also in browns, chocolate, &c. It is also used for silk, for several tints of lavender, violets, and as a ground for crimsons, &c.; but it is not used for cotton, having no affinity for that fibre.

Brazil wood.—*Bois de Pernambouc*, French; *Brazilienholz*, German.—There are several varieties of this wood, distinguished from one another by the name of the locality where they are obtained as Pernambuco, Santa Marta, Sapan, &c. By the dyers they are often all named peachwood, from an inferior sort much in use, and procured from Campeachy.

Fig. 36.



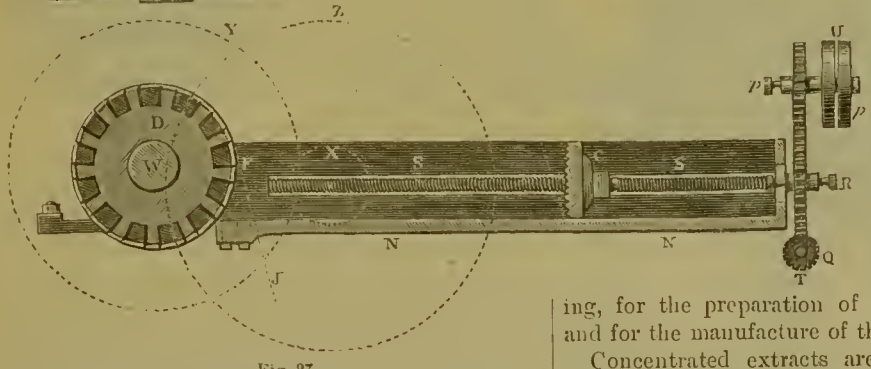


Fig. 37.

The Brazil wood tree, botanically termed *Cæsalpinia crista*, is a production of America. The Portuguese government early discovered its value, and made it a royal monopoly; hence was derived its obsolete and nearly forgotten name of *Queen-wood*. It mostly vegetates in dry places and amongst rocks; its trunk is large, crooked, and knotty.

The wood known in commerce as Pernambuco contains a larger amount of colouring matter than the others, and is most esteemed. It is hard, and is yellow when newly cut, but becomes red on exposure to the air. Lima wood is much the same in quality. Sapan wood grows in Japan, and stands next in value to the two before mentioned. It is not abundant, but is much prized for a certain shade of red, affording a clear, fine colour. Peach, or Nicaragua, sometimes called Santa Marta wood, is inferior in quality, but for some purposes is preferred, although the amount of colouring principle is not so great.

Brazil wood is distinguished from logwood by its paler colour, and by the precipitates which it gives with acetate of lead, protochloride of tin, and lime-water, which, instead of being violet as with logwood, are crimson. Both their infusions are rendered yellow by the addition of one or two drops of hydrochloric or sulphuric acid.

Brazil wood, or its colouring matter, is employed in dyeing in many ways.

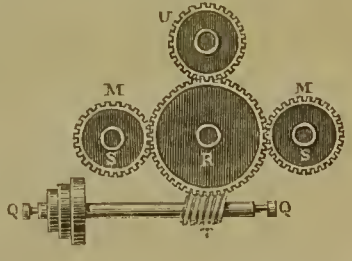
The wood itself, either reduced to shavings, raspings, or powder, serves for the production of red, rose-red, amaranth colour, and carmine red; sometimes the wood is mixed, in smaller or larger proportion, with garancin, for the dyeing of the so-called garancin colours. The wood is used in a mechanically divided state for the preparation of the decoction and concentrated extracts.

Decoction, or liquor of Brazil wood, is obtained by boiling, by means of steam, the raspings of the wood with from 18 to 20 times its weight of water, or by the exhaustion of the wood by displacement with boiling water. This liquor is used for dyeing, for the preparation of concentrated extracts, and for the manufacture of the Brazil lakes.

Concentrated extracts are now made having a specific gravity of 1·075, 1·162, or are even evaporated to solidity. The process used is much the same for all dyewoods.

*Extracts of the Woods.*—This manufacture is of comparatively recent date; it has sprung up with the more extensive use of the wood dyes, which in the raw state are not well fitted for calico printing.

Fig. 38.



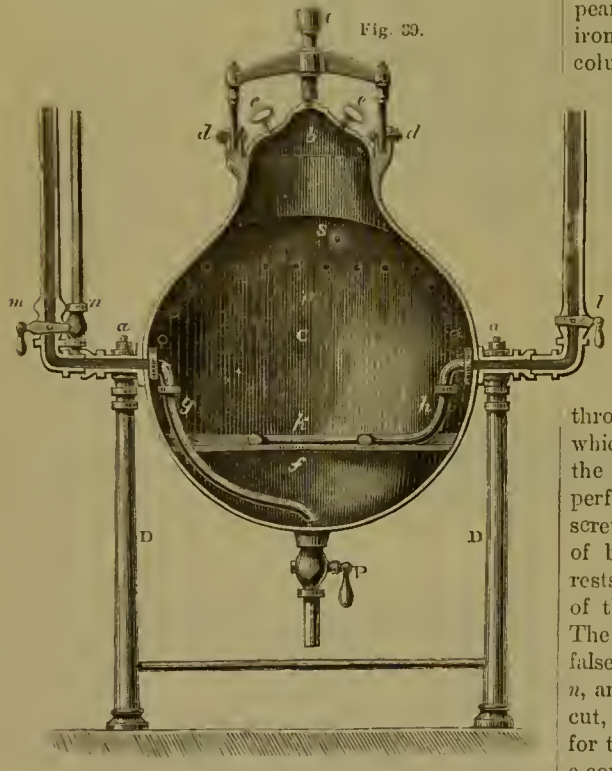
By means of suitable machinery (of which the engine shown in Figs. 36, 37, 38 may be taken as a convenient form), the woods are reduced to a coarse powder, or to small chips, cut generally in a direction perpendicular to their fibres. This operation requires a large amount of motive power.

The machine to be described was designed by Willmer, and is extensively used on the Continent. It is shown in plan in Fig. 36, and in longitudinal

section in Fig. 37. Fig. 38 displays the mechanism by which the wood is pushed forward to the cutting or rasping wheel. (The same letters apply to each engraving.) The driving wheels, z z, are put in motion by a band from a steam engine or water wheel; they work the cog wheels, x and y, and thus cause the axle, w, to revolve, which latter carries upon it the rasping or cutting cylinder, d. An iron bed, n b, serves for the reception of the wood to be rasped.

The wood is conveyed to the rasping cylinder by a constant pressure being exerted upon it by the plate, c, which is itself forced forward by the two screws, s s, parallel to the bed, n b n, upon which the plate, c, travels. (One of these screws is shown in Fig. 37.)

Fig. 39.




The movement of the screws, s s, is effected by the toothed wheels, m m (Fig. 38). upon the main wheel, r, which is itself moved by the endless screw, t, upon the axle, q. When it becomes necessary to refill the bed with wood, the plate, c, is rapidly drawn backwards by the cog wheel above r, which is started and stopped when desired by the loose and fixed pulleys, u, upon the axle, v *p*.

In order to prevent the blocking up of the cutters of the wheel, d, by pieces of wood fixing themselves upon the spikes of the cylinder, Willmer recommends that the pressure plate, c, be set parallel with the tangent line, f j, Fig. 37.

The wood will be ground much finer if a layer of long logs, a (Fig. 36), is disposed lengthwise on the top of the shorter pieces, as movement of the blocks under the rasp is thus rendered less easy.

The coarse powder or chips thus obtained are directly exhausted by means of water, or are left exposed in heaps, in a moist state, to a kind of oxidizing fermentation, whereby the solubility of the colouring matter is increased, and the subsequent exhaustion by water is rendered more easy.

It is important to carry on the exhaustion of the woods with the least possible expenditure of water, because the greater part of that vehicle has to be afterwards got rid of by evaporation. Some manufacturers carry on their operations in open tanks, applying water at 60° to 100° C.; but others prefer to work at a temperature above 100° C., and this has, of course, to be done in closed vessels.

The annexed sketches (Figs. 39 and 40) show the construction of steam-extraction vessels. The copper vessel, c, in which the extraction is effected, is pear-shaped, and rests upon two hollow wrought-iron axles, *a a*, supported between two cast-iron columns, d d, so that *c*, at the top of the figure, can, by turning the boiler round, be brought to where p stands in Fig. 39, and be reversed again if required. *b* is a manhole, hermetically closed by means of the screw, *c*, running through the frame, which is bolted to the neck of the pan at *d d*. In the interior of the pan is a false copper bottom, *f*, perforated with fine holes, and held in its place by screws at *i i*, fig. 40; above this is fastened a piece of brass wire-gauze of narrow gauge. On this rests the perforated worm tube, *k*, which by means of the pipe, *h l*, communicates with a steam-boiler. The pipe, *g*, which runs into the cavity, *f*, beneath the false bottom, is in connection with three tubes, *m*, *n*, and *o* (the latter is not, however, visible in the cut, being placed in front of and before *n*); *m* serves for the introduction of pure water. The pipes *n* and *o* convey the extracted dyestuff to barrels or vats by the steam pressure on the pan. The large tap, p, at the bottom of the pan, is for the removal of the dregs before the vessel is refilled with wood.

Fig. 40.



The mode of working is thus:—All the taps are closed, and the cap, *b*, lifted off by its handles, *c c*, and the finely-ground wood introduced. The tap, *p*, is opened, and water is then run into the pan through the tap, *m*, until it begins to flow out at the small tap, *p*; both taps are then closed, the cap, *b*, replaced, and secured by the screw, *c*. The steam tap, *l*, is next opened, and steam of the pressure of half an atmosphere allowed to enter and diffuse itself amongst the contents of the pan. In about half an hour the first extraction will be finished; during this time the level of the water must be kept between the two small taps, *p* and *s*.

On the conclusion of the operation the tap, *n*, is opened, and the dyestuff forced by the steam

pressure through the pipe, *g*, into the pipe, *a*, and thence to the barrels or vats. Water is again let into the pan, and a second extract made, which is sent after the first. A third extract is also made, but being far inferior in quality it is not mixed with the first two, but is forced through the pipe, *o*, to be dealt with separately. The dregs of the dye liquor are then drawn off by opening the tap, P, and after draining the boiler, the cover *b*, is taken off, and the exhausted dyewood emptied out by turning the pan upside down.

The evaporation of the liquors obtained from the exhaustion of the dyewoods with water is effected in various ways; sometimes vacuum pans are used, but they do not answer the purpose well for extracts which have to be concentrated above the specific gravity 1·134, on account chiefly of the difficulty experienced by the bubbles of aqueous vapour in escaping from a mass of viscous liquid; the evaporation is therefore most frequently carried on in double bottomed shallow pans heated by steam.

CATECHU—*Cachou*, French; *Kaschu*, German; *Catechu*, Latin—is an extract of the Khair-tree (*Acacia catechu* or *Mimosa catechu*) of Bombay, Bengal, and other parts of India. It was long regarded as of earthy origin, and bore the name of *terra Japonica*, or Japan earth.

As soon as the trees are felled the whole of the exterior white wood is carefully removed, and the interior coloured portion cut into fragments, which are placed in narrow-mouthed unglazed pots, and water added in sufficient quantity to cover them. Heat is then applied and maintained till the decoction is half evaporated, when, without being strained, it is transferred to a shallow earthen vessel, and further reduced two-thirds by boiling. It is next left at rest in a cool situation for a day, and is afterwards evaporated by the heat of the sun, being occasionally stirred during that time.

The extract thus prepared yields three varieties of catechu, viz.:—

*Pegu Catechu.*—The cutch or leaves met with in the trade in cakes weighing from 35 to 45 kilos., packed in large leaves. It is a dry, glossy, brownish-red or blackish-brown substance, of uniform texture throughout, and of a specific gravity 1·39.

*Brown Cutch.*—This is a less pure article; it is cast in sand or clay moulds.

*Brown Catechu.*—This kind of cutch is imported from Java, Singapore, Pegu (viâ Calcutta). It is sold in cubic-shaped cakes, packed in coarse bags, weighing from 35 to 40 kilos. per cake.

*Bengal Cutch* is obtained by a similar process to that above described from the fruit of the areca palm (*Areca catechu*), a tree widely spread over the tropical portion of Asia. It is met with in commerce in cubical cakes, each side measuring from 3 to 4 centimètres. The colour of Bengal cutch is brighter than that of the cutch shipped at Bombay (the mixed produce of the *Acacia catechu* and areca nut), the colour being chocolate brown, with deep and light coloured bands. It exhibits a dull appearance when broken, and is very dry and sandy, although sand is not necessarily present. Its specific gravity is 1·28.

*Yellow Cutch*, *Cubical Cutch*, or *Gambir*, is the extract obtained from the leaves of the *Uncaria gambir* and *Uncaria acida*, shrubs belonging to the family of the *Rubiaceæ*, tribe of the cinchonas, abundantly met with in Sumatra, Malacca, Pulo-Penang, Singapore, and the Sunda Islands. This kind of cutch, known very generally as "gambir," occurs in commerce in the shape of flat cakes, externally brown, internally yellow, fracture dull, taste bitter and astringent.

Catechu is often adulterated with various other astringent principles, or by the incorporation of clay, sand, ochre, and similar bodies. When other extracts have been mixed with it, it has often a dark and almost black colour, with a shining appearance, and occasionally feels glutinous or clammy.

The reactions of catechu are so varied, that it is now used for most compound colours, as black, brown, green, drab, and fawn; and its permanency renders it of high value.

It was first used for dyeing brown upon cotton, which is dyed by a very simple process. A little catechu is dissolved in boiling water, and a small portion of nitrate or sulphate of copper added to it; the cotton is wrought or steeped in this for an hour or two, and then taken out and wrought through a hot solution of bichromate of potash, which produces a brown of very great richness: it is washed from this, and then passed through a little soap and water, which softens the fibre.

CHICA is a red colouring principle, used by some Indian tribes for staining the skin, and is extracted from the *Bignonia chica* by boiling its leaves in water, decanting the decoction, and allowing it to cool, when a red matter falls down, which is formed into cakes and dried.

The Indian tribes of South America boil the leaves of the chica, and then produce a separation of the fecula by adding pieces of the bark of a tree, common to that part of the world, called *aryana;* it is then washed and formed into round cakes, about 2 inches thick and 5 or 6 inches in diameter, which are dried and considered fit for use. In this state the chica dye is now occasionally met with in commerce; it gives to cotton and woollen an orange-yellow colour.

INDIGO.—This valuable dyestuff is derived from a genus of leguminous plants found in India, Africa, and America, named *Indigofera*. Botanists have described about sixty species of this genus, all yielding indigo; but those from which it is usually obtained are the *I. anil*, the *I. argentea*, the *I. tinctoria*, and the *I. disperma*. It is also extracted from a tree very common in Hindostan (*Nerium tinctorium*), and from the woad plant (*Isatis tinctoria*), which is a native of Great Britain and of other parts of Europe. The colouring matter of these plants is wholly in the cellular tissue of the leaves, as a secretion or juice; not, however, in the blue state in which one is accustomed to see indigo, but as a colourless substance, which continues white so long as the tissue of the leaf remains perfect: when this is by any means

destroyed, oxygen is absorbed from the atmosphere, and the principle becomes blue.

In the East Indies, after having ploughed the ground in October, November, and the beginning of December, the seed of the indigo plant is sown in the last half of March or the beginning of April. A light mould answers best; and sunshine, with occasional light showers, are most favourable to its growth; when much rain falls, however, the plants grow too rapidly. Twelve pounds of seeds are sufficient for sowing an acre of land.

As soon as the young plants are sufficiently forward they are replanted in regular parallel rows, care being taken to weed out from the soil any useless parasitic plants.

The plants grow rapidly, and will bear to be cut for the first time at the beginning of July; in some districts even so early as the beginning of June. The indications of maturity are the bursting forth of the flower-buds and the expansion of the blossoms, at which period the plant abounds most in the dyeing principle; another token is taken from the leaves, the breaking across of which, when doubled flat, is accepted as a sign of ripeness; but this characteristic is somewhat fallacious, and depends much upon the poverty or richness of the soil.

The flower-buds are pulled off before they are fully developed, experience having taught that by so doing the leaves of the shrub become larger and yield more indigo, the colouring matter being chiefly in the leaves. In some localities the leaves, which have become bluish green, are pulled from the plant and gathered, but in most cases the entire plant is cut down close to the ground about the months of June or July, when the few flower-buds left have begun to open.

The first cropping of the plants is the best; after two months a second is made; after another interval a third, and even a fourth; but each of these is of diminished value. There are only two cuttings in America.

Two methods are pursued to extract the indigo from the plant: 1. By fermentation of the fresh leaves and stems; 2. By maceration of the dried leaves; the latter process being deemed most advantageous.

In the indigo factories of Bengal there are two large stone or brickwork cisterns, lined with cement, the bottom of the first being nearly on a level with the top of the second, to allow the liquid contents to be run out of the one into the other. The uppermost is called the fermenting vat or steeper; its area is 20 feet square, and its depth 3 feet; the lower cistern, called the beater or beating vat, is as broad as the other, but one-third longer. There are two rows of these tanks. Pure water in large quantity is an absolute requisite in an indigo factory. The water is brought by conduits into large ponds, and after having become clarified by settling, is conducted into large tanks, which are on a level with the masonry tanks just described.

The plant being cut down in the forenoon, is delivered in neatly made up bundles at the factory in the afternoon.

The cuttings of the plant, as they come from the field, are stratified in the steeper till it is filled within 5 or 6 inches of its brim. In order that the plant during its fermentation may not swell and rise out of the vat, beams of wood and twigs of bamboo are braced tight over the surface of the plants, after which water is pumped upon them till it stands within 3 or 4 inches of the edge of the vessel. It is essential that there should be left as little open space as possible, to insure the proper progress of the fermentation.

An active fermentation speedily commences, which is completed within fourteen or fifteen hours, a little longer or shorter, according to the temperature of the air, the prevailing winds, the quality of the water, and the ripeness of the plants. Nine or ten hours after the immersion of the plant the condition of the vat must be examined; frothy bubbles appear, which are at first white, but soon become grey-blue, and then deep purple-red. The fermentation is at this time violent, the fluid is in constant commotion, apparently boiling, innumerable bubbles mount to the surface, and a dense scum of a cupreous hue covers the whole. As long as the liquor is thus agitated it must not be interfered with, but when it becomes more tranquil it is to be drawn off into the lower cistern. Great care is required at this point of the operation, for should the fermentation be pushed too far the quality of the whole indigo is deteriorated; it is even better to cut it short, in which case there is indeed a loss of weight, but the article is better and the returns more profitable. The liquor now possesses a glistening yellow colour, which, when the indigo precipitates, changes to green. The average temperature of the liquid is commonly 85° Fahr.

As soon as the liquor has been run into the lower cistern men are set to work to beat it with oars or paddles, about 4 feet long, called "busquets." Paddle-wheels have also been employed for the same purpose. Meanwhile other labourers clear away the compressing beams and bamboos from the surface of the upper vat, remove the exhausted matter, set it to dry for fuel, clean out the vessel, and stratify fresh plants in it. The fermented plant still appears green, though it has lost three-fourths of its bulk in the process, or from 12 to 14 per cent. of its weight, chiefly water and extractive matter.

The liquid in the lower vat must be strongly beaten for an hour and a half, when indigo begins to agglomerate in flocks, and to precipitate. If the fermentation has been defective much froth arises during the agitation, which must be allayed with a little oil, and then a reddish tinge appears. If large round granulations are formed, the beating is continued to make them smaller, if possible. Should they become as small as fine sand, the water at the same time clearing up, the indigo is allowed quietly to subside. In case the vat was over fermented, a thick fat-looking crust covers the liquor, which does not disappear by the introduction of a flask of oil.

In such a case the beating must be moderated. Whenever the granulations become round and begin to subside, and the liquor clears up, the beating must be discontinued. The froth or scum diffuses itself spontaneously into separate minute particles, which moves about the surface of the liquor, and are marks of an excessive fermentation. On the other hand, a rightly fermented vat is easy to work; the froth, though abundant, vanishes as soon as granulations make their appearance. The colour of the liquor, when drawn out of the steeper into the beater, is bright green, but as soon as the agglomeration of the indigo commences it assumes the colour of Madeira wine; and speedily afterwards, during the beating, a small round grain is formed, the separation of which makes the water transparent, and causes the disappearance of all the turbidity and froth.

In order to hasten the precipitation, lime-water is occasionally added to the fermented menstruum in the progress of beating, but it is not indispensable, and has been supposed to deteriorate the indigo. Two or three hours after the agitation the supernatant liquor is run off, and by its condition affords a good indication of the success of both the processes. A labourer then enters the vat, sweeps all the precipitate into one corner, and empties the liquor into a spout leading into a cistern, situated beside a boiler, 20 feet long, 3 wide, and 3 deep. When all the deposit is once collected it is pumped through a bag, for retaining the impurities, into the boiler, and heated to ebullition, to check further fermentation, which would turn the indigo black. The froth soon subsides, and shows an oily-looking film upon the surface. The indigo is by this means not only freed from the yellow extractive matter, but enriched in the intensity of its colour and increased in weight. Some manufacturers, however, prefer retaining it at a moderate temperature throughout, and affirm that a deeper hue is produced.

From the boiler the mixture is run, after two or three hours, into a general receiver, called the *dripping* vat, or table, which, for a factory with twelve pair of preparation vats, is 20 feet long, 10 wide, and 2 deep, having a false bottom 2 feet below the top edge. This cistern stands in a basin of masonry, made water-tight with hydraulic cement, the bottom of which slopes to one end in order to facilitate the drainage. A thick woollen web is stretched along the bottom of the inner vessel to act as a filter. As long as the liquid passes through turbid it is pumped back into the receiver, but as soon as it runs clear the latter is covered with another piece of cloth to exclude the dust, and percolation is allowed to proceed spontaneously. Next morning the drained magma is put into a strong bag and squeezed in a press. The indigo is then carefully taken out, and cut with a brass wire into pieces of about 3 cubic inches each, which are dried either in a stove upon boards, or in an airy room upon shelves of wicker work. Or, the pasty and still very soft mass which remains upon the cloth is removed to small wooden boxes, perforated with holes, and lined inside with a stout and strong cotton tissue. These boxes having been filled, and a lid having been put on the top, likewise perforated, and so constructed as to fit *in* and not *on* the boxes, care being also taken to place a piece of cotton on the top, the boxes are placed under a screw press, and pressure having been gently and gradually applied, the water is squeezed out as much as possible, the liquid being again run into the filter tank to collect any indigo it may yet contain. The pressure having been withdrawn the boxes are opened, and the contents, shaped like blocks of soap, are placed in the drying room.

The drying should take place very slowly, and it takes from three to five days to dry the contents of each box. During the drying a whitish efflorescence appears upon the pieces, which must be carefully removed with a brush. In some localities, particularly upon the coast of Coromandel, the dried lumps of indigo are allowed to effloresce in a cask for some time, and when they become hard they are wiped and packed for exportation.

The other method of extracting the indigo from the plant differs from that described only in the first operations. Instead of putting the plant into the vat when newly cut, it is spread out to dry in the sun for two days, and then thrashed to separate the leaves from the stems. The former are kept until they have changed from a green to a bluish-grey or lavender colour, after which they are put into the first vat with warm water, and kept stirred till the leaves are so completely wetted as to sink. The liquor is then instantly let off into the beating vat, where it is treated as already described.

Indigo, as it occurs in commerce, is usually met with in cubical lumps or cakes, friable, more or less brittle, and of various shades of a peculiar deep blue, passing into violet purple. When rubbed with a smooth hard body it acquires a beautiful glossy and cupreous appearance, and always affords, on grinding, an intensely blue powder. Its specific gravity is sometimes greater, but at other times less, than that of water; this depends principally on its admixture with or freedom from foreign matters, but also upon the treatment of the paste in the operations of boiling, pressing, and drying. The best samples are those which are lightest in weight and most copper coloured.

The trade in Bengal indigo is chiefly carried on in Calcutta; its varieties are very numerous.

Coromandel indigoes of the best quality correspond to those of Bengal of medium value, and are met with in square masses, having an even facture, but are more difficult to break; indeed, these are harder to disrupture than any other variety. The inferior kinds are heavy, of a sandy feel, having a blue colour bordering on green, grey, or even on black; they are not unfrequently found having a greenish grey hue.

The productions of Madras have a grained rough fracture, and are of a cubical figure. The superior qualities have no rind, and are more light and friable than those of Coromandel. These kinds, when of the best quality, are very light, though not equal in this respect to the superfine blue of Bengal. The

middling classes have a very slight copper tinge. The colour of the inferior qualities is a dark or muddy blue, black, or even grey, and greenish.

The Manilla indigoes present the mark of the rushes upon which they have been dried. They are of a closer consistence and lighter hue than those of Madras, but not so compact as the produce of Bengal. The better qualities are often in flat and elongated masses, somewhat porous, and consequently light. Medium kinds are of a violet colour, but are inferior to the violet of Bengal.

Java indigo occurs in flat square masses, sometimes of a lozenge shape. The superior qualities appear as fine as the blue, violet, or red indigoes of Bengal, but they are not so in reality.

The superior classes of Egyptian indigo are superfine and fine violet blues. They are light, but their structure is not very compact, and they often contain sand. The squares are rather flatter than those of Bengal.

Senegal indigoes are of good quality, but contain more earthy matter than any others in the trade.

The indigoes of Guatemala, of the Caraccas, and of Mexico, are of various kinds. The best are a bright blue, remarkably light and fine. These are esteemed equal to the best Bengal. The inferior qualities are of a violet hue, but in general are more mixed than the Bengal kinds.

The Brazil indigoes are in small rectangular parallelopiped masses, or in irregular lumps, of a greenish-grey colour externally, having a smooth fracture, a firm consistence, and a cupreous tint of greater or less brilliancy.

The Carolina product is in small square masses, having a grey exterior. The best qualities have a dull copper colour, bordering on violet or blue. The common kinds are almost always of a greenish-blue; they are rarely found of a cupreous hue.

The following trade terms are in use in the indigo trade:—*Sandy indigo*, containing a large quantity of earthy matter. *Ribbon indigo* has bands of colour of different shades. *Spotted indigo. Burnt indigo*, this variety falls to pieces when pressed by the hand. *Large squared indigo*, cakes broken into large lumps. *Half broken indigo*, cakes broken into two pieces. *Coarse granulated indigo*, small lumps. *Cold indigo*, when the substance does not adhere to the tongue. *Fig indigo*, a very low quality used by makers of laundry blue.

LOGWOOD.—*Bois de Campeche*, *Bois bleu*, French; *Blauholz*, German; *Hæmatoxylum*, Latin.—This wood is obtained in great abundance in Jamaica and on the eastern shores of the Bay of Campeachy, and is imported into this country in small pieces or blocks. The wood from the two localities produces different qualities of dye; on this account the name of its habitat is affixed to each, and the two kinds are distinguished in commerce as Campeachy and Jamaica logwood. The former is superior to the latter, and consequently fetches a higher price in the market. The logwood tree is called by botanists *Hæmatoxylum campechianum*. In a favourable position it grows to a very large size. The bark of the tree is smooth and thin, and furnished with thorns, its leaves resembling those of the common laurel. The wood is very hard and close in the fibre, and is capable of taking on a fine polish; it is somewhat heavier than water, and consequently sinks when put into that liquid.

Logwood is very hard and close in the fibre. When used chipped in small pieces it requires long boiling to extract the colouring principle. To obviate this, the wood is now generally ground fine, by a machine such as that already described (see BRAZIL WOOD), by which means the operation is much facilitated. To avoid loss by dust in grinding, owing to the dryness of the wood, it is moistened by water, which greatly enhances the appearance of the wood, by producing a richer colour upon it, and does not affect its dyeing properties.

MADDER—*Garance*, French; *Faberröthe*, German—is the root of the *Rubia tinctorum*. It is common in the South of Europe and in many parts of the Levant, and is largely cultivated in Holland; it attains to about 3 feet in height, and has a long spreading fibrous root, which is the part used in dyeing. The best roots are of the size of a writing quill, or, at most, of the little finger. They are semi-transparent, reddish, have a strong odour, a smooth bark, and should be of two or three years growth. The root is taken from the ground, picked, and dried, in order to be ground and preserved. In warm climates it is dried in the open air; elsewhere, stoves are made use of. The stringy filaments and epidermis, termed *mulle*, as also the pith, are removed, leaving nothing but the ligneous fibres.

The roots are dried in a stove heated by a furnace, from which the air is allowed to issue only at the moment when it is judged to be saturated with aqueous vapour. Above the furnace flue, which occupies a great portion of the floor, are three gratings, on which the roots are arranged in layers of about 8 inches. At the end of twenty-four hours, those on the first grated floor directly above the stove are dry, and are taken away and replaced by those of the higher floors. The dried roots are then thrashed with a flail, passed through fanners similar to those employed for corn, and shaken upon a coarse sieve. The finer particles are again winnowed and passed through a still finer sieve. These operations are repeated five times, using sieves successively finer and finer, and putting aside each time the portion which remains on the sieve. The matter which finally passes through is rejected as sand and dust. After these manipulations, the whole of the fibrous substances remaining are cleaned with common fanners, and all foreign matters, which had not been before removed, are now separated. The roots are then divided into different qualities, for which a brass sieve is used, the meshes of which are from one-fourth to one-eighth of an inch in diameter. The finest portion is rejected, while the coarsest is considered of the best quality. These roots, thus separated, are carried into a stove of a construction somewhat different from the first. They are spread out in layers of about 4 inches in thickness, on large lattice-work frames, and the drying is known to be complete

when, on taking up a handful and squeezing, the roots break easily. On quitting the stove the madder is placed, still hot, into a machine, where it is cut small, and the portion of the bark reduced to powder is separated. This operation is repeated three or four times, after which resort is had to the bolter. The madder which passes through the brass meshes of the bolter is considered as common, and that issuing from the extremity of the bolter is called the flour. Lastly, the madder, after being subjected to these processes, is ground in a mill with vertical stones, and afterwards passed through sieves of different degrees of fineness. The madder of Alsace is reduced to a very fine powder, and it requires a much longer boiling to extract its tinctorial matter than is necessary for the "lizari" of the Levant. The prepared madders ought to be carefully preserved from humidity, as they readily imbibe moisture, in which case fermentation injures their colour. D'AMBOURNEY and BECKMANN consider that it is better to employ the fresh root of madder than that which has been stove-dried.

In commerce, the name of "lizari" has for a long time been restricted to the entire roots of the madder, while that of "madder" is applied to the pulverized roots.

Lizari is very little employed for the purposes of dyeing, and there is hardly any but that of Avignon which is met with in the markets of France.

*Dutch madder* has a strong and nauseous odour; its taste is sweet, but with a mixture of bitterness; its colour varying according to the marks, and passing from a brownish to an orange-red. The brownish-red tint, however, is applicable only to the "mulle" madder of each kind. The term "mulle," or "bilon," is applied to the inferior quality of madder, which consists of a mixture of the smallest roots, of the fibres and epidermis of the larger roots, of earthy matters, and of the refuse from the sieves.

In general, its powder is stringy, that is to say, its state of division is sufficiently large to exhibit the structure of the root. Exposed to the action of the atmosphere it readily absorbs moisture, and when, for the sake of ascertaining its quality, it is exposed to humid air, its orange-red becomes bright, rich, and deep. This madder, to use a commercial term, "works" more than others; that is, it presents more decided modifications of colour on exposure to moisture.

Dutch madder is either stripped or the contrary. In the first case, the roots have been freed from their epidermis, which gives greater brightness to the powder; in the second, they have been triturated without undergoing this operation, when the powder is of a more sombre hue. This madder cannot be used while fresh; it must at least be a year in the cask.

The *pale* powder, or that of the first year, having a yellow aspect, soon undergoes fermentation; the divided particles then unite with each other, agglomerate, and increase in volume to such a degree that, after from one to two years, the dilation is so great, that the bottoms of the casks present a very marked convex form. The madder is then so hard that, in order to take it out of the cask, a mallet or chisel must be used.

It keeps several years after having attained its greatest tinctorial power; but after about three years the layers which line the sides of the casks then begin to lose their brightness; the madder assumes a pale-brown colour, and enters into decomposition, the process of which is slow but certain; it subsequently becomes quite extinct, and the madder has a brown-red hue. When partially decomposed it may still be used for brown grounds or light colours; but when age has affected all the tinctorial principles it can only serve as "mulle." The term "grappe," signifying bunch, is employed when age has given consistence to the powder, and designates its state of agglomeration.

*Alsatian madder* has a penetrating smell and a bitter taste, and its colour varies from brown to bright yellow. It easily absorbs moisture from the atmosphere by exposure, and changes from yellow to a dark red.

It is not employed while fresh, and is in the best condition when about two years old.

*Madder of Avignon* is most generally used at the present time, and even preferred to the other kinds, because the dyer and the calico-printer find it easier to modify the reds according to wish.

The characters of this powder are—odour agreeable, slightly penetrating; taste, sweetish bitter: colour, either rose, bright-red, or brown-red, according to the roots employed in the preparation, and to the degree of mixture; state of division very fine; powder dry to the touch.

When submitted to the action of the atmosphere, it absorbs moisture less readily than the other species, but it does not work less, and subsequently affords a pale or very dark red, according to whether the powder operated on was "rosy" or "palus."

In Avignon, the name *Palus* is given to some tracts of land anciently covered with marshes; these grounds, enriched by animal and vegetable remains, are eminently suited for the cultivation of madder; the roots they produce being almost all red, and of a superior quality; whilst other kinds of soil yield rose-coloured roots.

The powder from the palus madder is of a rather unsightly red, but on drying it becomes blood-red, and the shade may be varied at pleasure.

The powder from the "rosy" is of a bright red, bordering a little upon yellow.

Avignon madder may be used immediately on leaving the mills; but that which has been preserved in casks for a year is decidedly preferable. It keeps well, and undergoes little or no fermentation; it does not cohere in a mass; after several years, however, it is decomposed with nearly the same symptoms as the other kinds: but is still fit for use.

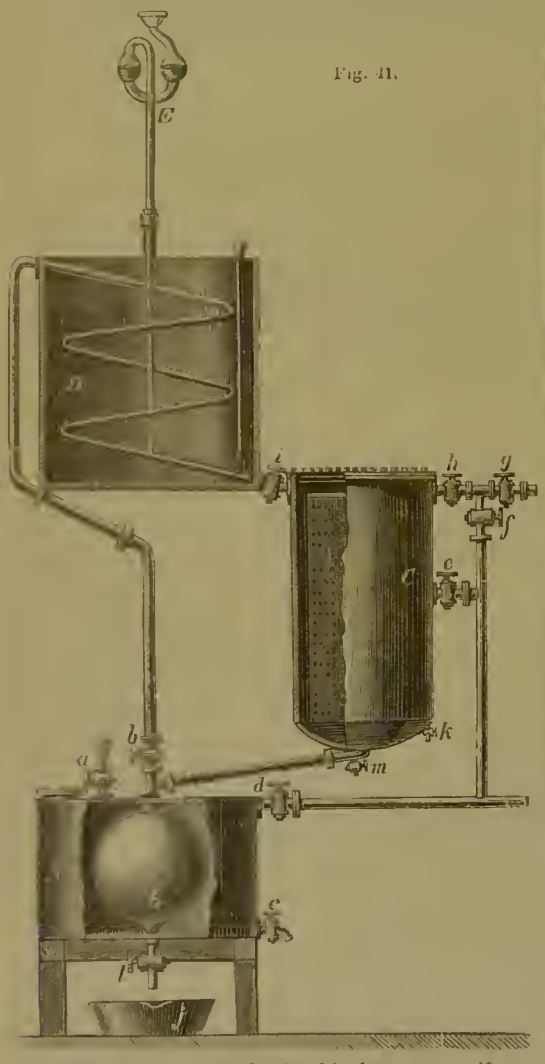
MALVACEÆ.—The petals of the plant known as *Althæa rosea*, belonging to the natural order *Malvaceæ*, contains a peculiar colouring matter, soluble in water and alcohol, but insoluble in ether. The

aqueous solution of the petals, freed previously from the calix and stamens, exhibits a violet-red colour, which is turned crimson by the addition of acids and green by alkalies. The alcoholic tincture of the leaves is purplish red, and leaves on evaporation a deepened residue, free from nitrogenous matter.

Cotton mordanted with iron is turned blue or bluish black by an aqueous infusion of the petals. With an aluminous mordant a violet blue, and with tin mordants a bluish violet, is produced.

Woollen fabrics, previously mordanted with bichloride of tin, assume a deep violet, and when

Fig. 41.




mordanted with iron a bluish black or grey; if mordanted with antimonic acid salts, a bluish violet is obtained.

Silk mordanted with tin salts takes a violet.

For calico printing the alcoholic extract suits better than the aqueous infusion. The apparatus employed by E. Kopp to prepare the alcoholic extract is shown in Fig. 41. The flowers are placed in a vertical wire-work cage, I, which is contained in the steam-jacketted cylinder, C. A pad of woollen cloth is then placed above the flowers, and the whole closed in by a tightly fitting iron plate. The spirits of wine are contained in the globular retort, B, placed in the cast-iron steam chest, A. The alcohol is volatilized by steam conveyed into A, through the tap, *d*. The alcohol vapour passes through the tap, *b*, into the condensing worm in the cold-water cistern, D, and is then forced under the pressure of the mercury contained in the pressure tube, E, through the tap, *i*, into the wire cage containing the flowers. The steam jacket, C, is at the same time heated by steam passing through the tap, *e*. The extract flows back into the retort, B, where it is caused to part with its spirit, which makes another circuit of the apparatus. The tap, *m*, serves to take samples. When the operation is judged to be completed, the taps, *d*, *e*, and *i*, are closed, and the tap, *a*, opened, in order to clear the steam chest, A, of steam. The taps, *f* and *h*, are next opened, in order by a momentary rush of steam to drive over the last remnants of alcoholic extract. The tap, *f*, is then closed, and the taps, *g* and *l*, opened, upon which the extract flows into the receptacle, *j*. The taps, *k* and *c*, are to run off condensed water when necessary.

Safflower; *Bastard Saffron*, *Carthamus*, *Carthamus tinctorius*. It is a native of Egypt, and the warmer climates of Asia. It has been cultivated in Europe, near Alsace, and also around Lyons. The Chinese have long known its use, and produce from it their finest red. The colour called by them *hing*, which is used by the Japanese ladies as a cosmetic, is made from it, and is kept in little porcelain cups similar to those retailed in this country as *pink saucers*.

It is obtained mostly from the East Indies and Turkey; the former is considered the best.

The *Carthamus tinctorius* is an annual plant, with an upright, firm, smooth stem, of a light grey colour. It grows to about 3 feet in length, when it divides into several branches, bearing leaves of an oval form, and edged with small spines. Each of the branches is terminated by a large flower-head, composed of several flowerets of a deep red colour. The plant is propagated by seeds, which are sown early in spring. It is from the flower that the dye is obtained; the richest colour is produced when the flowers are gathered before being fully blown. When collected, they are dried in the shade, and carefully preserved from any moisture, which would injure the colour.

As soon as the flowers are collected they are pressed between two stones, so as to deprive them of a portion of their juice; they are then washed several times with spring water, which contains a little common salt in solution. On being taken out of the water they are pressed between the hands, and then spread out on mats upon terraces, and allowed to dry slowly, being covered by mats during the day and exposed again at night. They are turned over from time to time, and when found to be properly dried are preserved for sale.

Safflower is found in the market in dry hard cakes. To prepare it for dyeing, a quantity of these cakes are steeped in clean cold water. Hard or spring water is preferable for this purpose. A cover is put upon the top of the cakes, and is subjected to a gentle pressure to keep them under the water. They

are allowed to lie in this condition till thoroughly wet and penetrated by the water, when the cakes expand and open up, under the influence of the moisture, into fine fibres. The whole is now removed by small quantities at a time, and placed upon a fine hair sieve, when water is passed through until it ceases to be coloured yellow. The washings are allowed to flow away, and the red fibres are then placed into a vessel sufficiently large to hold a gallon of water for each pound of safflower. To this water is added from 3 to 4 ozs. of carbonate of potash or soda for each pound of safflower; the whole is well stirred, and the stirring repeated every half hour. After six or seven hours the safflower has lost its red colour, and has acquired a dun tint; the whole is again passed through a hair sieve; but on this occasion the liquor passing through is carefully preserved, as it contains the dye; a little clean water is poured over every sieve-charge of the exhausted fibre, to wash out all colouring matter. The fibre is then pressed as dry as possible, and thrown away. The liquor has now a brownish-red colour, and is ready to dye cotton.

Turmeric.—Turmeric, or Indian saffron, is a yellow dye obtained from the roots of *Curcuma longa*. This plant is indigenous to the East Indies and other parts of Asia, and to Madagascar. It has been cultivated with some success in Tobago, and samples from that island have been found superior to that usually imported from India. Our supplies are brought from the East Indies, China, and Java; of these, the Chinese turmeric is the best.

The roots of the *Curcuma longa* spread far into the ground; they are long and succulent, and about half an inch in thickness. These roots are externally of a colour inclining to grey, but internally of a deep yellow colour; they are reduced to powder previous to being employed as a dye.

Weld or Wold is a biennial plant, called by botanists *Reseda luteola*. This plant is well known throughout Europe, and is indigenous to England; it is found growing wild in many parts of the country, and was once cultivated for its colouring produce in several counties of England, such as Kent, Herefordshire, and near Doncaster, in Yorkshire. It is very extensively cultivated around Paris, and in other parts of France. The plant, after being gathered, is carefully dried and tied up in bundles, in which state it is sold to the dyer.

Woad—*Isatis sativa*—is a plant known and used for the purposes of dyeing from the earliest times. The ancient Britons, when invaded by the Romans, are described as having their bodies stained with the colouring matter of this plant. It is cultivated in the Azores and the Canary Islands, in Italy, in Switzerland, in parts of Germany, Sweden, and in various districts of France. It is likewise indigenous to England, and is still cultivated in Lancashire. For many centuries it was a most important branch of British industry. It is still used as a dye for blue in woollen and silk stuffs, often, however, accompanied with indigo, the colouring matters of these substances being similar. A superior quality of this dye, which is principally produced in the South of France, is known in commerce by the name of *Pastel*.

The *Isatis sativa* is a biennial plant, having a large woody root, which penetrates deep into the ground; the stem is from 3 to 4 feet high, and about half an inch thick, divided into several branches. Three or four crops are usually obtained in one year. The plants are mowed with a scythe, and as soon as collected are washed in a stream of water and dried in the sun. This must be rapidly done, otherwise the woad will be impaired in quality. When dried, it is conveyed to a mill and ground into a smooth paste, which is laid in heaps, pressed close together, and covered to protect them from rain. If any crack appear in these heaps, care is taken to unite them, as that would also impair the quality of the woad. After remaining for a fortnight in heaps, the paste is rubbed together and formed into solid balls, which are pressed into a compact substance in wooden moulds and dried. Good balls are distinguished by their superior weight, and by having a violet colour within. These balls are further prepared for dyeing by being beaten with wooden mallets on a stone floor until they are reduced to a coarse powder, which is then heaped up in the middle of the apartment and moistened with water. Fermentation arises, and after about twelve days it is pretty well dried by being turned over, and then it is made into a heap for the use of the dyer.

Practical Operations.—For many of the receipts herein contained we are indebted to the *Moniteur de la Teinture*, *Reimann's Färber-zeitung*, *Muster-zeitung*, *Chemical Review*, *Dingler's Polytech. Journal*, &c., &c.

The dye woods may be used either (*a*) in the state of cold infusions, made by steeping the ground wood in water without the application of heat; or (*b*) in the state of a weak extract, made by putting upon a coarse flannel strainer 1 lb. of the ground wood for each gallon of liquid required, and pouring over the same boiling water till the liquor runs through nearly colourless; or (*c*) as a concentrated liquor or extract, marking from 8° to 24° Tw.; and, lastly (*d*) as a solid extract, formed by evaporating the liquid extract down to dryness. It must not be supposed that the properties of these four different states are identical. Where bright light shades are required, (*a*) or (*b*) will be found preferable; whilst for heavy shades, especially of sad colours, (*c*) and (*d*) should be employed. For all purposes where great concentration is needed (*a*) and (*b*) are, of course, inadmissible.

Barwood, camwood, and red sanders are always used in the ground state, the wood being put into the dye beck along with the goods.

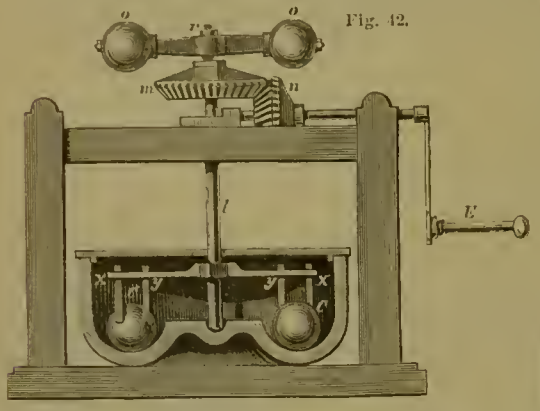
*To prepare Annotta.*—Into 2 gallons of water put 1 lb. annotta, 4 ozs. pearl-ash, and 2 ozs. soft soap, and apply heat, and stir until the whole is dissolved. When convenient it is best to boil the solution.

*To prepare Catechu.*—To 7 or 8 gallons of water put 1 lb. of catechu, and boil till all is dissolved; then add 2 ozs. of sulphate of copper, and stir, when it is ready for use. Nitrate of copper may also be used, taking one wine glassful of the solution

prepared as under:—To 1 part by measure nitric acid, and 2 parts water, add metallic copper so long as the acid will dissolve it, then bottle the solution for use. Perfectly distinct and valuable results may be obtained by grinding and extracting with cold water. Very fine greenish drabs are thus produced. The part insoluble in cold, if boiled, yields shades differing from those given by the decoction of the entire ware.

*Sulphate of Indigo.*—The indigo must be broken into small pieces about the size of hazel nuts, covered

Fig. 42.



with water, and left in steep for about twenty-four hours. It is then reduced to a fine paste in a mill. Fig. 42 is an indigo mill in which the colour is ground by cannon balls, *c*, which traverse an iron channel, being forced round by the pallets, *x*, *y*, firmly attached to the axle, *l*, by a framework. *e* is a handle which rotates the arrangement by means of the cogwheels, *n* and *m*. To secure regularity of motion, two heavy globes, *o o*, are screwed on the central axle at *r*, and made to rotate with it.

Another form of indigo mill is given in Figs. 43 and

Fig. 43.

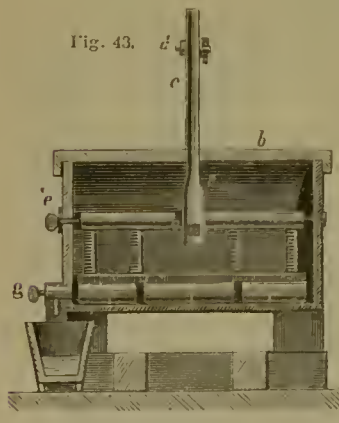
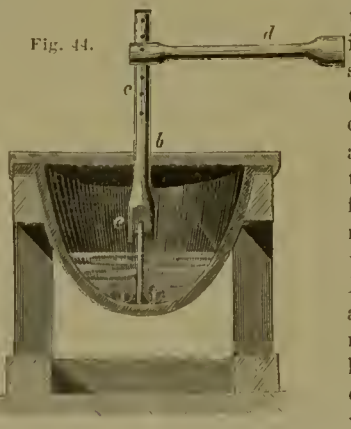


Fig. 44.



44. The vessel, *a*, is a four-sided iron tank, 2 feet 11 inches long, 19 inches broad, and 18 inches deep, cylindrical or rounded in the bottom, and resting upon gudgeons in a wooden frame. It has an iron lid, *b*, consisting of two leaves, between which the rod, *c*, moves to and fro, receiving a vibratory motion from the crank, *d*. By this arrangement a framework, *e*, can be made to vibrate about the axis, *e'*, and to impart its swing motion to six iron rollers, *f*, *f*, *f*, four inches in diameter, three of which are on each side of the frames. These triturate the indigo into a fine paste. This mill is capable of grinding 1 cwt. of indigo at a time. So soon as the paste is uniformly ground, it is drawn off by the tap, *g*, which had been previously stopped by a screwed plug, in order to prevent any of the indigo from lodging in the cock, and thus escaping the action of the rollers.

To make the sulphate of indigo: into 5 lbs. of the most concentrated sulphuric acid stir in by degrees 1 lb. of the best indigo, finely ground; expose this mixture to a heat of about 160° Fahr. for ten or twelve hours, stirring it occasionally; a little rubbed upon a window pane should assume a purple-blue colour.

This preparation is now sold in the market in the state of a paste, under the name of *Indigo Extract*, which is prepared by proceeding exactly as stated for sulphate of indigo, and then diluting with about 4 gallons of hot water, after which the whole is put upon a thick woollen filter, over a large vessel, and hot water poured upon the filter until it passes through nearly colourless; the blackish matter retained upon the filter is thrown away, and the solution passed through is transferred to a leaden vessel, and evaporated to about 3 gallons, to which is added about 4 lbs. chloride of sodium, and well stirred; the whole is again put upon a woollen filter and allowed to drain. The extract remains as a thin pasty mass upon the filter, and is ready for use.

The solution of indigo in sulphuric acid, without any further addition, is known as "chemic" or "sour extract." It is generally made from refined indigo. The paste extract, where more or less of the acid is neutralized by the addition of carbonate of soda, is called "sweet" or "free extract." Finally, if the sulphuric acid is entirely neutralized, the product is a dry powder, and is sold as "soluble indigo," occasionally as "free extract," and on the Continent very frequently as "indigo carmine"—a misleading name. In any extract of indigo it is essential that all the indigo should be perfectly dissolved. Any particles which may escape solution are very apt to produce specks on the dyed goods. It is also requisite that the green and brown colouring matters naturally present in the indigo should have been removed. The more acid extracts are employed in wool and worsted dyeing, whilst the more neutral modifications serve for silks.

These preparations of indigo are now very rarely employed for the production of pure blues, for which purpose they have been eclipsed by the aniline blues. Their chief scope is now in compound colours. There is hence the less need for a detailed account of the precautions necessary to obtain them in perfection.

*To make Red Liquor.*—Into 1 gallon hot water place 2 lbs. of alum; dissolve in a separate vessel 2 lbs. acetate of lead in 1 gallon of water; in a third vessel dissolve half a pound crystallized soda; mix all the solutions together and stir well for some time, then allow to stand over night; decant the clear solution, which is ready for use.

Caustic potash and soda can now be readily purchased on the large scale and of good quality. They are now consequently rarely prepared even in the largest dye works.

*To Make Lime-Water.*—Take some well and newly-burned limestone, and pour over it some water so long as the stone seems to absorb it, and allow it to stand; if not breaking down freely, sprinkle a little more water over it. A small quantity is best done in a vessel, as an old cask, in which case it may be covered with a board or bag. After being slaked, add about 1 lb. of this to every 10 gals. of cold water, then stir well and allow to settle; the clear liquor is what is used for dyeing. This should be made up just previous to using, as lime-water standing attracts carbonic acid from the air, which tends to weaken the solution.

*To Make Bleaching Liquor.*—Take a quantity of bleaching powder, and add to it as much water as will make it into a thin cream; take a flat piece of wood, and break all the small pieces by pressing them against the side of the vessel, then add 2 gals. of cold water for every pound of powder; stir well, put a cover upon the vessel, and allow the whole to settle. This will form a sort of stock vat for bleaching operations.

*To Make a Sour.*—To every gallon of water add 1 gill of sulphuric acid, stir thoroughly; goods steeped in this should be covered with the liquor, as pieces exposed become dry, which deteriorates the fibre; if left under the liquor, the cloth is not hurt by being long in the sour; but on being taken out every care should be taken to wash out the liquor thoroughly, otherwise the goods will be made tender.

*To Make Cochineal Liquor or Paste.*—Put 8 ozs. ground cochineal into a bottle, and add to it 8 ozs. by measure ammonia and 8 ozs. water; let the whole simmer together for a few hours, when the liquor is ready for use.

*To Make Iron Liquor.*—See Acetates, or small quantities may be made as follows:—Put pieces of iron, or filings, into pyroligneous acid, and allow it to stand for several days, stirring occasionally; a gentle heat assists the action.

*To Make Nitrate of Iron.*—Place in a good-sized cask, holding not less than 130 gals., one quarter ton of clean copperas, free from damp. Pour upon it 130 lbs. of double aquafortis at 65° Tw., and stir up the whole well that the acid may touch every portion of the copperas. To avoid injury from inhaling the fumes, the cask should stand in an open shed or under a draught-hood connected with a chimney. In the evening stir up again, not with a violent circular motion, but seeking to turn over all the copperas from the bottom. The next day stir in the same manner both morning and evening, and again in the morning of the third day. The third night the copperas will be found totally dissolved, at most a few pounds remaining. The liquid is let down with water to about 80° Tw., stirred up, let settle, and bottled off. Like all varieties of nitrate, or rather nitro-sulphate of iron, it must be screened from light and preserved from extremes of heat and cold. This quality is well adapted for dyeing a blue with prussiate upon cotton yarns and unmixed cotton pieces. For mixed piece goods it should not be used.

For a nitrate of iron for blacks the same process may be followed, but the double aquafortis should be reduced to 120 lbs. per quarter ton of copperas. Some dyers prefer to add to black nitrate of iron a proportion of brown acetate of lead (crude sugar of lead), which should not reach 70 per cent. of the weight of the copperas originally employed.

A nitrate of iron for sky-blue, or for conversion into green by topping with a yellow dye, may be made by letting down common aquafortis with water to 32° Tw. To this clean scrap iron is then gradually added as long as it is dissolved with the escape of an orange gas. The solution, when saturated and cold, stands about 43° Tw.

For full bloomy royal blues on the cotton warps of mixed piece goods the following formula may be used:—Dissolve 16 lbs. nitrate of soda in 13 gals. of water. Weigh out 20 lbs. of oil of vitriol, and add it by degrees, along with as much clean scrap iron as is needed. Do not let the mixture get too hot. This nitrate should not be made in large amounts at once, as it soon deposits a sediment, especially in hot weather. The presence of muriatic acid is very objectionable in any nitrate of iron employed to dye mixed goods, as it has the tendency to throw the iron upon the wool or worsted.

The following compound, which is an "iron alum," is used and recommended by some dyers:—Dissolve 78 lbs. red oxide of iron in 117 lbs. sulphuric acid; let down with water; add 17 lbs. of sulphate of potash, and let crystallize.

*To Make up a Blue Vat.*—Take 1 lb. of indigo, and grind in water until no grittiness can be felt between the fingers; put this into a deep vessel—casks are generally used—with about 12 galls. of water; then add 2 lbs. copperas and 3 lbs. newly-slaked lime, and stir for fifteen minutes; stir again after two hours, and repeat every two hours for five or six times; towards the end the liquor should be of a greenish-yellow colour, with blackish veins through it, and a rich froth of indigo on the surface. After standing eight hours to settle, the vat is fit to use.

Preparation of Spirits.—Although most if not all the mordants required in dyeing may be purchased, it is very important for the dyer to be acquainted with their preparation.

*Single Muriate of Tin.*—Dissolve grain-bar tin, previously feathered or granulated, in commercial muriatic acid, till the specific gravity rises to 50° to 60° Tw. The strength of the acid to begin with is generally 32° Tw. In some establishments it is

let down with water to 20° or 22° Tw. before adding the tin, in which case a greater amount of metal must be dissolved to bring the solution up to any required strength. It contains from 1 to 2 ozs. of tin to the lb.

*Double Muriate of Tin* is sometimes erroneously supposed to be a persalt. It is merely a solution of the protochloride, like single muriate, but of greater strength, ranging from about 70° to 120° Tw., and containing from 2½ to 5 ozs. metallic tin per lb. The weaker qualities, at from 70° to 90° Tw., are used in woollen dyeing; and the stronger, which of course contain a relatively smaller proportion of acid, for cotton dyeing.

Some of the most useful mixtures of muriate of tin with other acids are the following:—

*Bancroft's Scarlet Spirit.*—Mix spirits of salt at 32° Tw., 2 lbs; oil of vitriol, 3 lbs.; and dissolve 14 ozs. in the mixture. This spirit is in less demand than formerly, as the grain and lac scarlets dyed with it generally take a somewhat brownish shade.

*Yellow and Orange Spirit.*—Mix oil of vitriol, 2 lbs.; water, 2 lbs. When cool add the mixture to 5¾ lbs. good double muriate. On this spirit W. Crookes remarks that the more tin and the less free acid exist in the muriate the more the cloth will exhibit a beautiful greenish reflection if held up to the light and viewed horizontally.

*Another Yellow Spirit.*—Spirits of salts, 3 parts; oil of vitriol, 1 part; water, 1 part; feathered tin, as much as it will take up. Care must be taken that whilst the tin is dissolving the heat shall not rise above 60° Fahr.

*Amaranth Spirit.*—Spirits of salt, 95 lbs.; oil of vitriol, 5 lbs.; mix, and dissolve 4¾ lbs. of tin. This preparation is used by some dyers for reddish-violet wood shades.

*Scarlet Finishing Spirit.*—Take 3 pints muriate of tin at 54° Tw., and add 2 ozs. oxalic acid, dissolved in hot water enough to bring the mixture to 40° Tw.

It is used for raising cochineal or lac scarlets which have been previously grounded with the "bowl spirit" or "nitrate of tin" to be mentioned below. Some dyers replace half the oxalic acid directed with tartaric acid. In some establishments this spirit is employed for scarlets at once, without the previous grounding with nitrate of tin, and without tartar. This method is used for hard worsted trimmings. For softer materials the strength of the muriate may be preferably 60° or 70° Tw. This variation is especially adapted for cochineal oranges, maizes, and similar shades.

*Another Receipt.*—Add to 4 gals. muriate of tin at 54° Tw. 1 pint oil of vitriol, previously mixed with 3 pints of water, and allowed to cool. Then dissolve 1 lb. of oxalic acid in a gallon of water, and add the solution to the other ingredients. Tartar is required when this spirit is used in dyeing scarlets.

*Puce Spirit.*—Take 4 gals. muriate of tin at 70° Tw., and add 2 gals. of sulphuric acid previously let down with water to 28° Tw., and let cool.

*Oxalate of Tin.*—The mordant commonly so named is really a muriate of tin, to which oxalic acid, oxalate of potash, and generally sulphuric acid, have been added in very variable proportions.

It may be made by adding 1 oz. of oxalic acid, dissolved in hot water, to 1 gal. of the "puce spirit," just mentioned. It is employed as a royal blue finishing spirit for blooming blacks, as a scarlet spirit with cochineal or lac, and as an orange spirit, with cochineal and flavin or young fustic. Where extra brightness is required, the oxalic acid may be increased to 2 ozs. per gallon. Such an increase is not required for topping blacks.

With the exception of the stronger kinds of double muriate, the above-mentioned preparations are used in woollen dyeing, and are not suited for vegetable fibre.

Tin crystals, the solid muriate of tin, are obtained by evaporating down the strongest solution of the metal in muriatic acid till it crystallizes. The crystals are generally sold in stoneware jars, containing from 2 to 3 cwts., and should be protected as far as possible from contact with the air. They generally form a somewhat milky solution with water, which, however, becomes clear on the addition of a few drops of muriatic acid. They are sometimes adulterated with sulphate of magnesia or sulphate of zinc, a fraud which is easily detected by dissolving a small portion of the sample in pure muriatic acid, diluting with distilled water, and adding a little of a solution of the chloride of barium. If any sulphate is present a white turbidity is occasioned. If it be required to find the quantity of tin present in either tin crystals or single or double muriate it may be ascertained as follows:—Weigh out 100 grs. of the sample, and mix them with 20 ozs. pure water, and half an oz. of muriatic acid. Dissolve in hot water 83½ grs. pure bichromate of potash, and fill a burette with the solution. Drop this liquid from the burette into the solution of tin, which gradually turns green. Continue adding the bichromate solution very gradually until a drop taken out, and placed upon a white saucer, gives a yellow colour when tested with a drop of the solution of acetate of lead. Every degree of the burette consumed until this effect is produced represents 1 gr. of metallic tin in the weight of the sample operated upon.

Tin crystals are used for very much the same purposes as the stronger kinds of double muriate. They are also frequently employed along with a mixture of nitric and muriatic acids, or with chlorine gas, in preparing the persalts of tin, stannic chloride or tin perchloride, in a state of greater or less purity.

The sesquisalts of tin, which we next mention, are used both for animal and vegetable substances.

*Nitrate of Tin*, otherwise known as "scarlet spirits" and "bowl spirit," is prepared as follows:—Into a large clear bowl is put a known weight of so-called "single aquafortis," a kind specially prepared for this use, marking from 32° to 34° Tw., and perfectly free from sulphuric acid and from nitrous fumes. It contains, however, a certain proportion of hydrochloric acid, which is absolutely necessary for this use. Grain-bar tin of the best quality, and in the

rod, not feathered, is weighed out in the proportion of 1 lb. metal to 8 lbs. of acid. A number of these rods, varying according to the temperature and to the make of the acid, are put in and allowed to dissolve. In average weather four or five rods may thus be entered. In a short time, if the operation is rightly conducted, the liquid, which was previously colourless, "turns," that is, assumes a deep amber colour. The remainder of the tin is then gradually added, taking care that the action does not become too violent, and that no bubbles of orange-coloured gas are formed. In hot weather one or two bars are quite sufficient in the outset, whilst in frost eight or ten may be needful. If the temperature is very high half a pint of nitrate of tin from a previous lot should be added to the aquafortis at the outset, and the spirit may then be started with a handful of clean and dry feathered tin. Rods are then gradually added when the process has been fairly commenced.

This spirit has an amber colour. It should mark from 58° to 60° Tw., and contain 2¼ to 2½ ozs. of tin per lb. It is used both for woollen and cotton dyeing.

*Purple Spirit* (for certain woad purples upon woollens and worsteds).—Take nitrate of tin as above described, freshly made and good. Set the bowl containing it in a larger vessel of hot water, and add as much grain-bar tin in the rod as it will dissolve. It should stand at about 80° Tw.

*Aniline Spirit.*—Mix 5 gallons of single aquafortis at 32° Tw., with half the quantity of muriatic acid at the same strength, and enter gradually 12 lbs. of best grain bar tin, not feathered. Do not let the mixture get very hot. This spirit contains nearly 2 ozs. metallic tin to the 1 lb. of mixed acids, and if properly worked will be of a dark amber colour. It gives a white precipitate, which quickly turns black. The resulting liquid, sometimes mixed with oxalic acid, is used by some dyers for dyeing cochineal scarlets, and gives good results.

The persalts of tin, used chiefly in cotton and silk dyeing, are prepared either by dissolving the metal in a mixture of nitric and muriatic acid in which the latter predominates, or by dissolving tin crystals in a similar manner. The compounds obtained in these methods are apt to vary. The nitric acid is never entirely expelled, and appears to combine with some of the tin and to modify its action. Further, a part of the tin generally remains in a state of protosalt (stannous chloride). To obtain a pure perchloride of tin (stannic chloride), the most effectual process is to dissolve tin crystals in the very smallest possible quantity of muriatic acid, and to pass chlorine gas through the solution till a drop taken out and mixed with a solution of the perchloride of mercury (corrosive sublimate) no longer gives a white precipitate which turns black on standing. A pure perchloride thus obtained can be either used alone as a mordant or may be mixed with the muriate (protochloride) in any required proportion, and the effects thus obtained can always be exactly reproduced. Still there are cases where the spirits made with mixtures of nitric and muriatic acids produce peculiar and desired effects, and we therefore give a selection of receipts for their preparation.

*Red Cotton Spirits.—*

| | |
|---|---|
| Muriatic acid at 32 Tw., | 7 gals. |
| Double aquafortis at 62 Tw., | 1 " |
| Water, | 1 " |

Tin in the rod is then gradually added till 6 lbs. have been dissolved. Avoid excess of heat. The amount of muriatic acid may be reduced as low as 3 gallons, different proportions producing a spirit suitable for different colours.

A somewhat different spirit is made with—

| | |
|---|---|
| Muriatic acid at 32° Tw., | 17 gals. |
| Double aquafortis at 62° Tw., | 3 " |
| Tin enough to raise the strength to 54° Tw. | |
| Bichrome, | 2 ozs. |

It is chiefly used for the cotton warps of mixed goods which are to be dyed in aniline colours, or are to receive certain compound shades, such as clarets, from the woods.

Various preparations are used as mordants, which consist chiefly of stannic chloride or tetrachloride of tin, formerly known as bichloride. They figure in technological works and in trade catalogues under many names, such as "composition," tin-solution, oxymuriate, permuriate, nitro-muriate, &c.

*Barwood Spirit—*

| | |
|---|---|
| Muriatic acid, | 5 gals. |
| Double aquafortis, | 1 " |
| Tin, 1 oz. per lb. of the acids. | |

*Plum Spirit—*

| | |
|---|---|
| Muriatic acid, | 6 gals. |
| Double aquafortis, | 1 " |
| Tin, 1½ oz. per lb. | |

The so-called plum tub is made by adding from 1 pint to 1½ pint of plum spirit to a gallon of strong logwood liquor. It dyes silks and cottons without any further preparation, and was formerly in great demand, but since the introduction of the aniline violets and purples it has fallen very much into abeyance as far as silks are concerned.

*Purple Cotton Spirits—*

| | |
|---|---|
| Muriatic acid, | 5 lbs. |
| Double aquafortis, | 1 " |
| Tin, 2 ozs. per lb. | |

*Pansy Spirit—*

| | |
|---|---|
| White argol, | 5 lbs. |
| Granulated tin, | 5 " |
| Muriatic acid, | 5 " |

Add 15 lbs. oil of vitriol, previously diluted with a gallon of water, and finally add very gradually 2 lbs. of double aquafortis.

Chemical analysis throws very little light upon the practical value of these compound spirits, the mere amount of tin being of less importance than its condition. The greater or less speed with which the tin is added to the acid, and the temperature attained, greatly affect the quality of the result. If the heat be too great, a part of the tin is often deposited in an insoluble and useless state, and even

when this does not happen, its affinity for the fibre is often destroyed. Spirits which have been injured in these manners are said to have been "fired."

*Aceto-nitrate of Chrome.*—Select a stone-ware bowl holding 30 litres, and set it upon supports in the open or under a draught-hood, so that it may be gently heated. Put into it 3 kilos. of chromate of potash in coarse powder, 4·4 litres of boiling water, 2·6 litres of nitric acid, at 36° B. Mix well together, and add gradually 0·72 litre of white glycerine at 28° B., and 4·28 litres acetic acid at 7° B. When all is dissolved, pour into a double-bottomed pan, and heat rapidly to a boil by means of steam. This is kept up until the liquid appears of a pure green in thin layers. It is then allowed to cool in a stone-ware bowl, decanted, and the deposit of saltpetre is washed with 0·8 litre of cold water, and the washings added to the first part of the liquid.

*For Copperas.*—See *Iron Salts, ante.*

*For Blue-Stone*—sulphate of copper.—See *Copper Salts, ante.*

In making solutions of these salts, such as copperas, blue-stone, chrome, &c., there is no fixed rule to be followed. A quantity of the crystals are put into a vessel, and boiling water poured upon them, and stirred till dissolved. Some salts require more water than others when saturated solutions are wanted; but in the dye house a certain degree of saturation is not essential, and therefore there is always used ample water to dissolve the salt. In all cases, however, the proportions are known, so that the operator, when adding a gallon or any quantity of liquor to the dye bath, knows how much salt that portion contains. From a half to 1 lb. per gallon is a common quantity.

*To Remove Oil Stains.*—When oil spots are upon goods, and so fixed or dried in that steeping in an alkaline lie will not remove them, rub a little soft soap upon the oil stain, and let it remain for an hour, then rub gently with the hand in a lather of soap, slightly warmed, and then wash in water; for cotton, a little caustic lie will do equally well for removing the oil, but the soap is the preferable process, and seldom fails. Benzine is largely used by dress dyers to remove recent stains; care must be taken to keep it from fire of any kind, as its volatility is exceedingly great. It is essential that all oil or grease be removed before dyeing.

*To Remove Iron Stains.*—Take a little hydrochloric acid in a basin or saucer, and make it slightly warm, then dip the iron stain into the acid for about one minute, which will dissolve the oxide of iron; the cloth must be well washed from this, first in water, then in a little soda and water, so as to remove all trace of acid. A little oxalic acid may be used instead of hydrochloric, but more time is required, and with old fixed spots it is not so effective. The same precautions are necessary in washing out the acid, as oxalic acid dried in the cloth injures it.

*To Remove Mildew from Cotton.*—Proceed with the stains by rubbing in soap or steeping in a little soda, washing, and then steeping in bleaching liquor the same as in the process of bleaching, or by putting a wine-glassful of the stock liquor as prepared above in 1 pint of water, afterwards wash, and pass through a sour, and wash.

*To Remove Indelible Ink Marks.*—Steep the marking in a little chlorine water, or a weak solution of bleaching liquor, for about half an hour, then wash in ammonia water, which will obliterate the stain; the goods to be washed from this in clean water. Or they may also be removed by spreading the cloth with the ink mark over a basin filled with hot water, then moisten the ink mark with the tincture of iodine, and immediately after take a feather and moisten the parts stained by the iodine with a solution of hyposulphite of soda, or caustic potash or soda, until the colour is removed, then let the cloth dip into the hot water; after a while wash well and dry.

*To Detect Animal and Vegetable Fibres.*—In order to detect the different fibres in fabrics, they may be first gently heated with caustic soda, which will only dissolve wool and silk, while cotton or linen is left behind. If the alkaline liquid, on the addition of a few drops of acetate of lead, assumes a brown or black colour, wool is present. Another portion is then treated with a cold neutral solution of zinc chloride, by which only the silk is dissolved. Or, treat the fabric with tetrachloride of tin heated to from 130° to 150° Fahr., when the cotton and linen become black, and wool and silk remain unchanged.

*To Detect Mixed Fabrics of Cotton and Wool.*—Dip a piece of the suspected cloth in bleaching liquor; after a little the woollen turns yellow and the cotton white, and consequently may be easily distinguished.

*To Detect Cotton in Linen.*—The piece to be tested is boiled to remove all dressing, and then dried; a portion of the piece is put into common vitriol for about one minute, it is then taken out, washed in water several times, and then in a weak solution of soda or potash, and all gummy matter formed is removed by gentle rubbing; by this process the cotton is dissolved out and the linen remains, or what portion of the cotton is not dissolved becomes opaque white; the linen is transparent, and is thus easily detected. By comparing the portion of cloth immersed with a similar portion not tried, the quantity of cotton present may be easily estimated. Or, take a small piece of the cloth, boil in water and dry; then take 3 parts, by weight, of sulphuric acid, and 2 parts of crushed nitrate of potash; the dry piece of cloth is put into this for six or seven minutes, and then washed from this till there is no taste of acid, dry at a gentle heat; then put it into a mixture of ether and alcohol, which will dissolve the cotton and not the linen. If the piece be weighed before putting into the ether and alcohol, and after, the quantity of cotton in the fabric may be thus ascertained.

The presence of cotton in linen may also be ascertained by dipping the fabric into a solution of one part of magenta in 20 parts of spirits of wine and washing with water, which will remove the colour completely from cotton, but not completely from linen. Instead of magenta, an alcoholic solution of

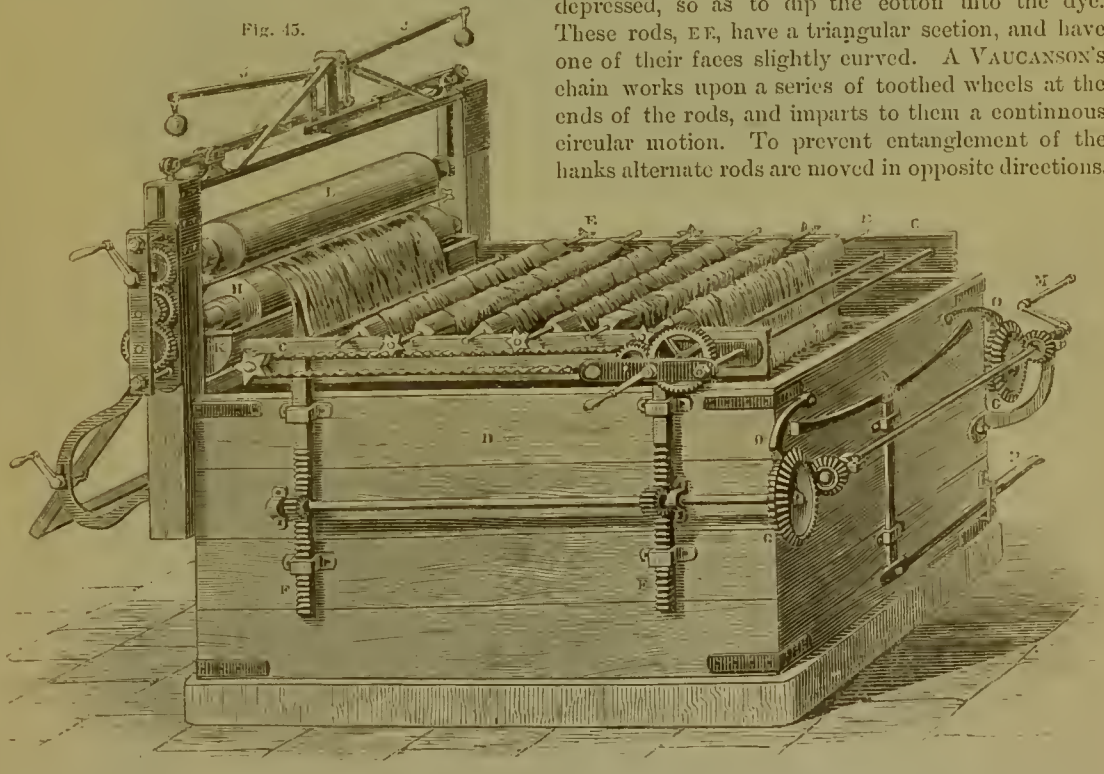
anrin may be used, which after washing the yarn or cloth with a concentrated solution of soda-crystals, produced a pink on linen, while cotton becomes colourless.

*Cotton and Wool.*—Take a small piece of the cloth and boil in caustic soda, when the wool will be dissolved and the cotton remain. If the threads have been previously counted, their relative mixture may be thus ascertained.

*Cotton with Silk and Wool.*—Put a piece of the cloth into chlorine water or bleaching liquor. The cotton is whitened by the liquor, and the silk and woollen become yellow. These changes will be easily distinguished by the use of a small pocket lens.

*Another Method.*—Take a small piece and unravel the threads and inflame them; the cotton burns away freely, with little or no black charcoal; the woollen and silk shrivel up, leave a black charcoal, and give a strong smell.

Fig. 45.



Dyeing Cotton Yarn.—Cotton is generally brought to the dye house in bundles of 5 lbs. or 10 lbs., made up of heads, each head having 10 hanks, except when the yarn is very coarse, when each head has only 6 hanks; or very fine, when each head has 20 hanks. The number of heads indicates the grist of thread, called "the number." Thus, 10 lbs. of No. 60 will have 60 heads of 10 hanks, or 30 heads of 20 hanks. These heads are made up into spindles of 18 hanks by the dyer, and through each spindle is tied a piece of stout thread or twine, termed a band; the bundle, when banded, is divided into four or six quantities, and rolled up and tied into bundles for boiling. Thus, No. 60 will give 35 spindles and 12 hanks, equal to 36, and will be rolled up into 6 sixes, or all sixes, as it is termed, or 4 nines, 10 lbs. being invariably named a bundle.

After banding, cotton is boiled in water for two or three hours until thoroughly wet. The bundles are then loosed, and each roll of yarn is put upon a wooden pin, about 3 feet in length and about 1½ inch thick, six pins or sticks forming a bundle, or four sticks, according to the division made by the bander.

An ingenious machine for dyeing skeins has been devised by M. Deshayes. A rectangular dye beck, D (Fig. 45), which may be constructed of wood, metal, or brickwork, and is heated by steam forced into it, contains the dye liquor. By means of rackwork, FF, the frame, CC, which holds the rods with the bundles of yarn, is at pleasure elevated and depressed, so as to dip the cotton into the dye. These rods, EE, have a triangular section, and have one of their faces slightly curved. A Vaucanson's chain works upon a series of toothed wheels at the ends of the rods, and imparts to them a continuous circular motion. To prevent entanglement of the hanks alternate rods are moved in opposite directions.

After a sufficient immersion the frame is raised and the hanks drained, after which they are wrung by passing them between the two cylinders, L, H, the one of which is of wood, the other of vulcanized india-rubber. The lower cylinder is provided with a vessel, K, running beneath it to catch the waste dye liquor.

After passing through the wringing cylinders the yarn is again arranged to undergo a second dyeing. The operation is repeated until a sufficient depth of colour has been attained.

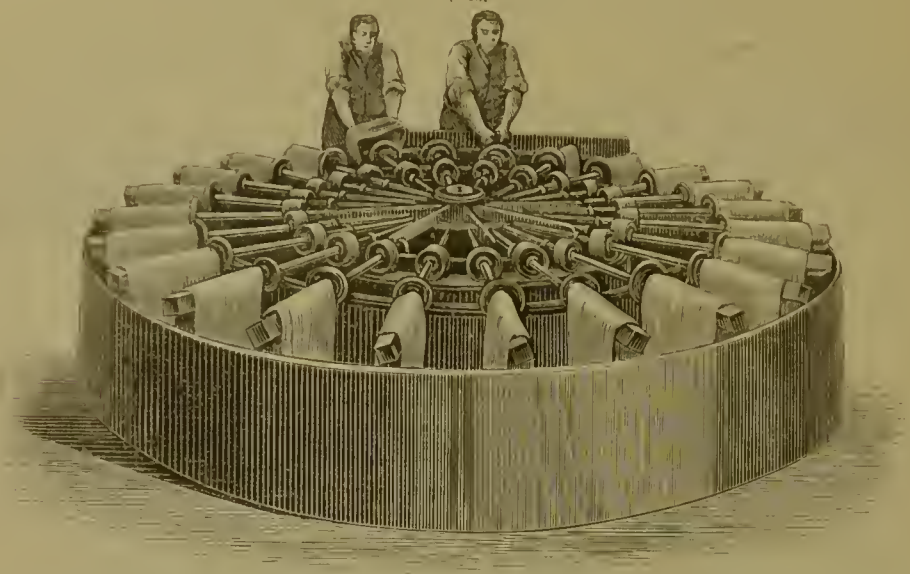
CC is the movable frame, EE are the rods which hold the yarn, FF the rackwork set in motion by the gear work, GG, moved by the handle, M. L, H, are the wringing cylinders, pressure upon which is maintained by the levers, J J.

The frame, C C, is lowered on lifting the arm, N,

by treading on the lever, P, when the pauls, o o, set free the wheels, G G. The diagonal frame at the end of the dye beck is for the purpose of tilting the vessel, K, and so returning the surplus liquor into the bath.

After dyeing, the hanks are washed. A machine for this purpose, which is of almost universal use in Germany, is the circular washing machine invented by C. G. HAUBOLD. A glance at Fig. 46 will enable the reader to understand its mode of working.

Fig. 46.

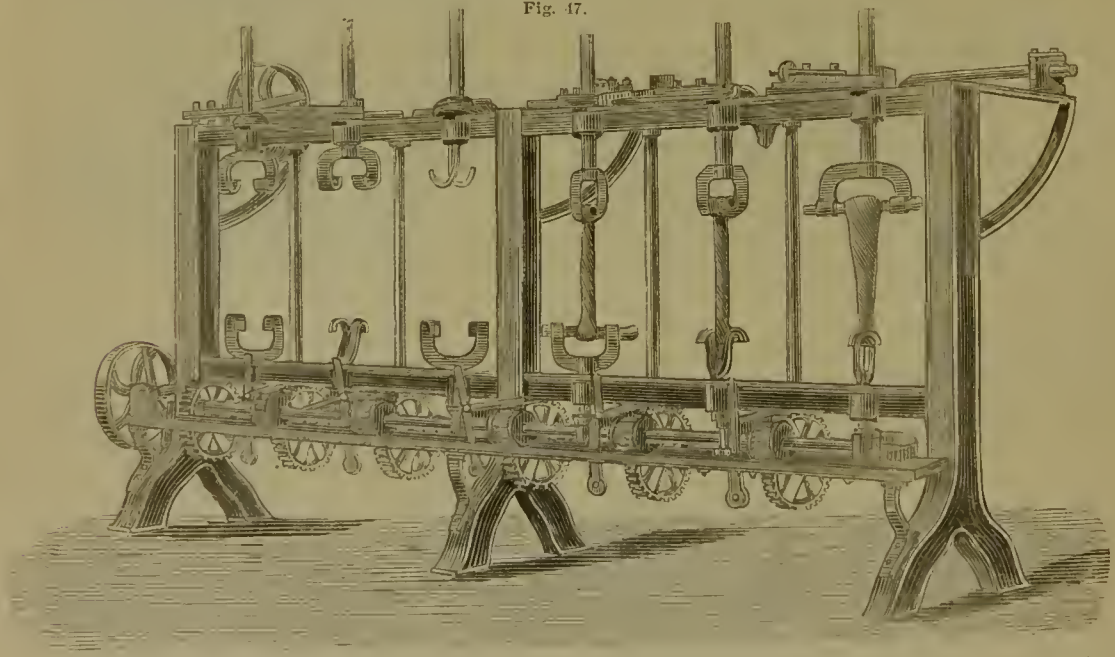


Pure water flows in at the end at which the hanks are taken off, and runs away, bearing with it the surplus dye, at the place where the workman feeds the machine.

A wringing machine is shown in Fig. 47.

To dry hanks rapidly, especially in the case of wool, the hydro-extractor is much used. The particular arrangement shown in Fig. 48 is due to BURDIN, who has done much to perfect this kind of machine.

Fig. 47.

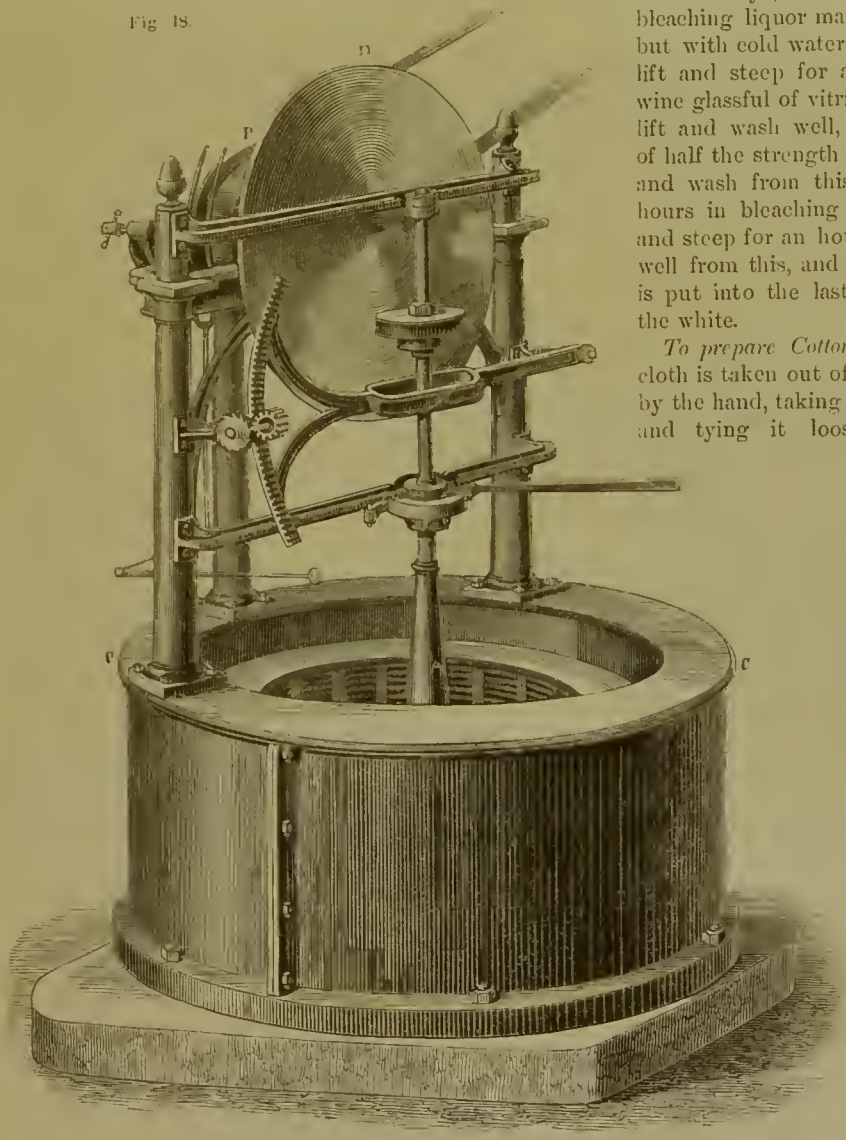


A plane circular disc, D, is set in rapid rotation by a band on the pulley, P. A friction roller, running lengthwise in a horizontal groove, bears upon the surface of the disc, and can be made to exercise a greater or less resistance by bringing it nearer to or farther from the centre. The central axle, A, carries a second friction roller, which also bears against the disc, D. By means of these two friction rollers the speed of rotation of the axle, A, can be regulated with great nicety.

The axis, A, carries a cage, into which the stuffs to be dried are put. It is then set in rapid rotation, upon which, by centrifugal force, the water is dashed through the interstices of the cage into the outer envelope, C C.

If the colour to be dyed be dark, such as brown, black, orange, deep blue, &c., the yarn is at once ready for the dyeing operation; but if for light shades, such as pink, sky-blue, &c., it must be bleached previous to being dyed, which is done

Fig 18.




thus:—A vessel sufficiently large to allow of the cotton being wrought in it freely without pressing is filled about two-thirds with boiling water; add 1 pint of bleaching liquor from the solution made up as described above for every gallon of water in the vessel, then work the yarn in this for half an hour. Into another vessel of similar size, filled two-thirds with cold water, add a wine glassful of sulphuric acid for every 2 gals. of water; stir well, and then put the yarn from the bleaching solution into this and work ten minutes, and then wash from this until all acid is removed.

This, in general, will produce a white of sufficient purity for all light shades.

But if the cotton is to be finished white, in that case the process is conducted as under:—

The yarn when banded is boiled for three hours in caustic lye, either potash or soda, made by adding 1 gill of the caustic lye, prepared as described above, for each gallon of water in the boiler; wash well from this lye, and lay the yarn to steep in a bleaching liquor made up as in last receipt, but with cold water; after four or five hours lift and steep for an hour in a sour of 1 wine glassful of vitriol to the gallon of water, lift and wash well, then boil again in a lye of half the strength of the first for two hours, and wash from this, and steep again four hours in bleaching liquor; wash from this, and steep for an hour in a clean sour; wash well from this, and dry. A little smalt blue is put into the last washing water to clear the white.

*To prepare Cotton Cloth for Dyeing.*—The cloth is taken out of the fold and hanked up by the hand, taking the end through the hank and tying it loosely, technically termed "kinching;" it is then steeped in old alkaline lye overnight, which loosens and removes the oil, grease, and dressing which it has obtained in weaving; it is then thoroughly washed in clean water. Where there is a dash wheel it should be used for this washing.

From these liquors often fermenting with the paste in the cloth, this process has been technically termed the "rot steep."

If the colours required upon the goods be dark, no other preparation is necessary; but if light, the cloth has to be bleached, which is done by boiling after the "rot steep" in caustic lye, of the strength of one gill of stock lye to the gallon of water, for three hours; wash out the boil, and steep in bleaching liquor for six hours, same strength as given for yarn; wash, and steep an hour in a strong sour of one wine-glassful of sulphuric acid to the gallon of water; wash well from this before drying or dyeing. If the cloth be very heavy, one operation may not be enough; in such cases proceed as at the beginning, by boiling, steeping, and souring. In bleaching cloth for dyeing, care has to be taken that it is

all equally white, otherwise it will show in the colour.

If the goods be old, and have been previously dyed, and if the shade required be a deep shade, and the colour of the goods light, in that case nothing is generally required but steeping to remove any grease or starch; but if the dye upon the cloth be dark, the best method is to proceed as if they were grey goods, and subject them to a process of bleaching. The quantity of water used in the operation is simply as much as will allow the pieces or the yarn ample room to be put under the fluid easily without pressure.

Receipts.—In the following receipts, where not otherwise specified, the quantity of wares is for 10 lbs. of cotton, whether yarn or cloth. Of course any quantity may be dyed by proportioning the dyeing materials to the fabric; but when small articles are dyed—such as ribbons, gloves, handkerchiefs, or a dress—a little more of the stuff may be used without affecting the general tint of the colour, as small quantities cannot be dyed with the same economy as on the large scale. Where washing is referred to, it is always in cold water, unless hot be mentioned.

*Common Black.*—Steep the goods in a decoction of 3 lbs. sumach while it is hot, and let them lie over night; wring out and work for ten minutes through lime-water, then work for half an hour in a solution of 2 lbs. copperas. They may either be washed from this, or wrought again through lime-water for ten minutes—the former gives the preferable shade, but must be well affused; work them for half an hour in a warm decoction of 3 lbs. logwood, adding a half-pint of chamber lye; before entering the goods, lift and raise with 2 ozs. of copperas in solution; work ten minutes, then wash and dry.

*Jet Black.*—The goods are proceeded with exactly as last; but along with the logwood is added 1 lb. fustic, and finished as above.

In both these blacks, if 3 pints iron liquor be used instead of the copperas, or in part mixed with the copperas, it makes a richer shade of black, but copperas is most generally used; if mixed, use half the quantity of each.

*Blue Black.*—Dye the goods first a good shade of blue by the vat, and then proceed exactly as for common black; but should the blue be very deep, as is often the case, then half the quantity of the materials given above will suffice.

*Spirit Brown.*—The goods are dyed first a spirit yellow, and washed; they are then wrought for half an hour in a decoction of 2 lbs. lima or peach wood and 1 lb. logwood; lift up and add 3 ozs. alum in solution, and work fifteen minutes; wash and dry. By varying the proportions of logwood and lima wood, a variety of shades can be produced.

*Mordant Brown.*—Dye a yellow, then work for half an hour through a decoction of 2 lbs. lima wood and 8 ozs. logwood, lift and raise with 2 ozs. alum in solution; work for fifteen minutes, and wash and dry.

This method is well adapted for cloth goods, is better than the spirits, and more easily performed by the non-practical man. The spirit brown is best for yarn.

*Cinnamon Brown.*—Dye a dark spirit yellow, and work for twenty minutes in 3½ lbs. lima wood and half a pound logwood; then raise, by adding 2 ozs. of alum in solution; wash in cold water, and dry.

*Vvanterin Brown.*—Dye a spirit yellow, and then work for twenty minutes in a decoction of 1 lb. lima wood and 1 lb. fustic; lift and raise by adding half-pint red liquor; work ten minutes in this; wash in cold water, and dry.

*Fawn Brown.*—Take 1 part annotta liquor and 1 part boiling water; stir well, and work the goods in this for ten minutes; wring out and wash in two waters; then work for twenty minutes in a decoction of 2 lbs. fustic and 1 lb. sumach; lift and add 3 ozs. copperas in solution; stir well, and work for twenty minutes longer; wash from this in two waters; then work for twenty minutes in a decoction of 8 ozs. lima wood, 8 ozs. fustic, and 4 ozs. logwood; lift and raise with 1 oz. alum; work ten minutes; wring out, and dry.

*Catechu Brown.*—Work the goods at a boiling heat for two hours, or steep for several hours if the liquor is allowed to cool, in 2 lbs. catechu, wring out, and then work for half an hour in a hot solution of 6 ozs. bichromate of potassa; wash from this in hot water. If a little soap be added to the washing water, the colour is improved.

Any depth of shade of brown may be dyed by repeating the operation.

*Catechu Chocolates.*—Dye a brown, as last, then work fifteen minutes in a decoction of 1½ lb. logwood; lift, and add 3 ozs. alum in solution; work ten minutes longer; wash out, and dry.

By this process a great variety of browns and chocolates may be produced, both by using different quantities of logwood, and by different depths of brown before the logwood is applied.

*Chocolate or French Brown.*—Dye a spirit yellow, then work for half an hour in a decoction of 3 lbs. logwood; lift, and raise with half a pint of red liquor, and work ten minutes longer; wash and dry.

Another shade of deeper chocolate will be obtained by adding 1 lb. fustic with the logwood.

*Catechu Fawns.*—Work the goods fifteen minutes in hot water, to which has been added 2 pints of the catechu; wring from this, and work fifteen minutes in hot water, in which has been dissolved 1 oz. of bichromate of potash; wash from this, and dry.

*Catechu Fawns—Another method.*—Work in the solution of catechu the same as last; wring out, and then work for fifteen minutes in warm water, to which has been added 2 ozs. acetate of lead previously dissolved; wash in cold water, and dry.

*Catechu Fawns—Another method.*—Work for fifteen minutes in warm water, to which has been added four pints of catechu; lift, and add 2 ozs. copperas in solution, and work for other fifteen minutes; wash from this in one tub water, and finish through warm water, in which as much soap has been dissolved as will raise a lather, and dry out.

*Common Red.*—Put the goods into a decoction of 3 lbs. sumach as soon as possible after being made, and let them steep till the liquor is cold, say

over night; wring out, and work for an hour in red spirits diluted to from 2° to 2·5° Twaddle's hydrometer, or about one gill spirits to each gallon water; wring out, and wash well, and make a decoction of 3 lbs. lima wood and 1 lb. fustic; work the goods in this for half an hour at a heat that the hand may be held in without pain, lift up and raise by adding 1 gill red spirits; return the goods, and work fifteen minutes longer; wash out, and dry.

*Barwood Red.*—To a decoction of 2 lbs. sumach add a wine-glassful of vitriol, and steep the goods in this decoction for at least six hours; wring out and work in spirits, diluted to 2·5° Tw., for an hour; wring out and wash, then pass through a tub of warm water; put 10 lbs. of barwood into a boiler with water, and bring it near to the boil, into which the goods are entered and wrought amongst the wood grains for about three-quarters of an hour; lift out, wash, wring, and dry. Deeper shades may be dyed by using greater quantities of stuffs in each operation.

*Common Crimson.*—To a decoction of 3 lbs. sumach, the goods steeped in it over night, and then spirited at 2° Tw.; wash, and work through a decoction of 3 lbs. lima wood and 1 lb. logwood for thirty minutes, then raise with a gill of red spirits; work for fifteen minutes more; wash out, and finish.

By using only lima wood without logwood, a beautiful red crimson is obtained, and by varying the proportions and quantities, a great diversity of tints will be dyed by the same proportion of sumach and spirits.

*Light Straw.*—To a tub of cold water add 4 ozs. of acetate of lead, previously dissolved, work the goods through this for fifteen minutes, and wring out; into another tub of water add 2 ozs. of bichromate of potash; work the goods through this ten minutes, wring out, and pass again through the lead solution for ten minutes; wash, and dry.

*Leghorn.*—Proceed and finish exactly as last, but along with the chrome add a half-pint annotta liquor.

Different depths and tints may be obtained by using more or less of these stuffs, without varying the mode of working.

*Annotta Orange.*—Heat the annotta solution to working heat—about 140° Fahr.; work the goods in this for twenty minutes; wring tightly out, in order not to lose much stuff; wash in a couple of waters, and dry.

If this colour is passed through water made to taste sour by an acid, a very red orange, bordering on scarlet, is produced; but the hue is very fugitive.

*Logwood Blue.*—Dye first a light-blue with the vat, then lay in a hot decoction of 2 lbs. sumach for several hours, and keep working for fifteen minutes through water, to which has been added 1 pint acetate of alumina (red liquor) and 1 pint acetate of iron (iron liquor); wash from this in two tubfuls of hot water, then work twenty minutes in a decoction of 2 lbs. logwood; lift, and raise with half a pint of red liquor; work ten minutes longer; wash, and dry.

*Fustic Green on Yarn.*—Dye a vat blue, wash and wring, and then pass through the acetate of alumina at 6° Tw.; wash through a tub of hot water, and then work for twenty minutes in a decoction of 4 lbs. fustic; lift and raise with 2 ozs. alum in solution, work fifteen minutes, wash, and dry.

*Bark Green on Cloth.*—The goods after being cleaned, not bleached, are wrought for ten minutes in red liquor at 7° Tw., wrung out, and passed through a tub of hot water, and then wrought for half an hour in a decoction of 3 lbs. bark, lifted, and raised with half a pint red liquor, and wrought ten minutes longer, then lifted and drained. Into a tub of cold water add 5 gallons of "chemie"—neutralized sulphate of indigo; work the yellow in this for twenty minutes, wring out, and dry. Of course any depth of shade may be made in this way by varying the quantity of stuff used.

*Fustic Green on Cloth.*—Work the goods in acetate of aluminium at 6° Tw., and dry in a stove or hot chamber; then wet out in hot water, and work for twenty minutes through a decoction of 3 lbs. fustic; lift, and raise with 2 ozs. alum in solution; work fifteen minutes; wring out, and then work in the "chemie" neutralized sulphate of indigo; wring out, and dry.

*Green with Prussian Blue.*—Dye a good Prussian blue, same way as sky, according to the depth of green required; and then work ten minutes in acetate of alumina at 6° Tw.; wash in a tubful of warm water, and work for half an hour in a decoction of 3 lbs. fustic; lift, and raise with 2 ozs. of alum in solution; work ten minutes longer; wash, and dry.

Bark may be substituted for fustic in this green. If so, the bark should not be wrought very warm; and thus a finer tint is obtainable.

*Sage Green.*—Dye a Prussian blue, same as sky, and work ten minutes in a solution of 2 lbs. alum; wring out, and work fifteen minutes in a decoction of 1 lb. fustic; lift, and add a pint of the alum solution formerly used; work ten minutes, and then wash and dry.

*Olive or Bottle Green.*—Dye a good shade of Prussian blue, then mordant by working ten minutes in acetate of alumina at 7° Tw.; wring out, and wash in hot water; work for half an hour in a decoction of 3 lbs. of fustic and 1 lb. of sumach; then add half a pint iron liquor, and work fifteen minutes; then wash in one tub water having 2 ozs. alum dissolved in it, and dry.

*Olive or Bottle Green—Another method.*—Work the goods in red liquor at 7° Tw., wash in warm water, and work half an hour in a decoction of 3 lbs. bark and 1 lb. sumach; lift, and add half a pint iron liquor, work fifteen minutes; wring out, and then work fifteen minutes in the "chemic;" wring out of this and dry.

*Olive Green.*—Dye a Prussian blue, then work for ten minutes in red liquor at 6° Tw.; wash in hot water, and work in a decoction of 3 lbs. bark and 1 lb. logwood; lift, and raise with half a pint of red liquor, and work ten minutes; wash from this, and dry.

A great variety of shades of green may be obtained by varying the proportions of bark and logwood. Fustic may also be used instead of bark.

If the goods be yarn, a light vat blue may be dyed instead of the Prussian blue, and proceeded with afterwards in the same manner as above.

*Puce or Lilac.*—Work for an hour in red spirits made down to 2° Tw.; wring out, and wash, then work half an hour in a decoction of 3 lbs. of logwood at working temperature, about 140° Fahr.; lift up, and add 1 gill red spirits, work for twenty minutes; wash from this, and dry. Half a pint of red liquor, or 2 ozs. alum, may be added to the logwood as raising, instead of red spirits.

*Another Method.*—Work the goods for fifteen minutes in red liquor at 7° Tw.; wring out, and wash in one tub warm water, then work for half an hour in a decoction of 2 lbs. of logwood at working heat; lift, and raise with half a pint red liquor, or 2 ozs. alum; work ten minutes in this, and wash in a tub of lukewarm water; wring out and dry.

*Light Purple or Adelaide.*—The goods are laid in a decoction of 2 lbs. sumach, wrung out, and wrought half an hour through the "spirit plum;" wring out and wash in clean cold water till no taste of acid is felt on the goods, and dry.

When working with the "spirit plum," it is best to take the plum liquor into a tub or separate vessel, and work the goods in this, returning the liquor afterwards to the plum tub.

*Another Method.*—The goods are laid in 2 lbs. sumach, wrung out, and wrought for twenty minutes in red spirits at 2° Tw.; wash well from this, then work in the spirit plum in the same manner as last; wash out till no taste of the acid is on the goods, and dry.

*Purple.*—Steep in 2 lbs. of sumach till cool; work in red spirits at 2° Tw. for an hour, and wash in cold water; then work for half an hour in decoction of 3 lbs. of logwood at working heat; then lift, and add 1 gill of red spirits, and work for ten minutes more; wash in cold water, and dry.

A variety of purple shades may be dyed by this process, by slightly varying the proportions of the stuffs. If a browner tint is required, give a little more sumach; if a bluer tint, less sumach, and increase the logwood, and raise with half a pint red liquor, or 2 ozs. alum, instead of red spirits.

*Lavender or Peach.*—Work the goods for twenty minutes through the spirit plum, wring out, and wash in clean cold water till no taste of acid is perceived, and dry.

*Logwood Lilac or Puce.*—Dye the goods a good shade of Prussian blue, then work for fifteen minutes in a decoction of 1 lb. of logwood at working temperature; lift up, and add 4 ozs. alum; work ten minutes, and then wash in cold water, and dry.

*Another Method.*—Dye a sky blue, then in a tub of warm water add 1 gal. alum plum, and work in this fifteen minutes; wring out, and dry.

*Safflower Lavender.*—Dye the goods a sky-blue, then dye a safflower pink on the top of the blue, with 1 lb. safflower; but in dyeing the pink, the sulphuric acid must be added to the safflower liquor previous to the blue being entered into it, otherwise the alkali of the safflower will destroy the blue.

It need hardly be added, that different depths of colour and different hues will be obtained by varying the shade of blue and the quantity of safflower. Deep blue with a little safflower give a lilac, or puce; while a light blue, with 4 lbs. of safflower, will give a peach colour.

*Safflower Lavender—Another Method.*—Dye a pink with 2 lbs. of safflower, then proceed and dye a sky blue over this, and finish exactly as described for sky blue.

Of course the remarks made on last receipt, in reference to different shades, apply equally to this method; but more safflower is required by this method than the other.

*Common Drab.*—Work the goods for fifteen minutes in a decoction of half a pound sumach; lift, and add 1 oz. copperas in solution and work for fifteen minutes; wash out in a tub of cold water, then work for fifteen minutes in a decoction of 4 ozs. fustic, 2 ozs. lima wood, and 1 oz. logwood; lift, and raise with 1 oz. alum in solution; work ten minutes longer, wring out, and dry.

A great variety of shades can be produced by this means, varying the proportion of the lima wood, fustic, and logwood; and different depths, by varying the quantities of sumach and copperas.

*Olive Drab.*—Work fifteen minutes in half a pound sumach, then add 1 oz. copperas, and work in this for fifteen minutes; wash in one tub water, and work in half a pound fustic for twenty minutes, and raise with 1 oz. alum; work ten minutes, and dry out.

*Drab.*—To a tub of hot water add 1 pint of annotta, which gives a light salmon colour, then proceed with this exactly as last for olive drab; or, by varying the quantities in last operations, a great variety of drabs may be dyed.

*Stone Colour.*—Work the goods twenty minutes in a decoction of 1 lb. sumach; lift and add 1 oz. copperas in solution; work fifteen minutes, and wash in one tub cold water; then work ten minutes in warm water, to which half a pint alum plum has been added; wring, and dry.

This gives a reddish tint; but if this tint be not required, the alum plum may be dispensed with, using half an ounce alum in the water.

*Catechu Stone Drab.*—Work the goods for fifteen minutes in 2 pints catechu in hot water; lift, and add 2 ozs. copperas in solution; work for fifteen minutes, and wash in one tub of water. Into another tub of warm water add a decoction of 2 ozs. logwood; work the goods in this for ten minutes; lift, and raise with half an ounce alum; work ten minutes longer, wring out, and dry.

*Catechu Drab.*—Work the goods for fifteen minutes in hot water, to which has been added 1 pint catechu, then lift, and add 1 oz. copperas; work ten minutes, and wash out and dry.

*Fast Black to bear milling* (100 lbs.)—Boil in water 8 lbs. of solid extract of logwood and 1¾ lb. extract of bark, and boil the yarn in this one and a half to two hours, and longer if needful. Enter in a cold beck of 1 lb. chromate of potash and 12½ ozs. of blue vitriol, and give it six or seven turns. Then

return to the extract beck, in which 2½ lbs. soda have been dissolved meantime; give five turns, let stand a while, give two more turns, and lift. This beck is used at a hand heat. Then add 2 lbs. copperas; re-enter, and give five more turns.

*Sumach Black* (50 kilos).—Prepare with 10 kilos. of sumach over night at a boil; enter in a fresh beck of 7 kilos. copperas and 1 kilo. precipitated chalk; work cold for an hour, take out, and air. Make up a fresh beck with 3 kilos. quicklime, and work till it appears an even brown all over; rinse well, and dye in a fresh beck at 75° C. with 25 kilos. of Domingo logwood and 5 kilos. bark; sadden, lastly, in the same beck with 1 kilo. copperas.

*Black for Yarns, not to Smear* (5 kilos.).—Boil 1 kilo. sumach, and steep the goods in the boiling liquid for six hours; lift, steep thirty minutes in black liquor; lift, and return to the sumach beck, give five turns, and re-enter in the black liquor; expose to air for two hours. Dissolve 170 grms. chromate of potash, and make up a cold beck; work in this for ten minutes, and rinse. Extract 1 kilo. logwood and a quarter kilo. bark in boiling water; make up a beck at 62° C.; work in this for fifteen minutes, lift, rinse, and dry.

*Fine Black on a Vat Ground* (12½ kilos.).—Give a blue in the vat, take out, and treat with 3 kilos. sumach; take through nitrate of iron, and then through weak lime-water without rinsing; and, lastly, dye in logwood.

*Blue Black for Cotton Velvets* (10 lbs.).—Take through a beck of soda at a boil, which if cold would mark 2° B., rinse, and steep over night in the decoction of 2 lbs. myrobalans, lift, drain, and work for fifteen minutes in iron liquor at 5° B. Work then for fifteen minutes in a cold beck of 1 lb. alum and 1 lb. blue vitriol; rinse, and dye at 50° C. with 2 lbs. logwood and half a lb. bark for fifteen to thirty minutes.

To soften the goods take them through an emulsion of half a lb. olive oil and 2½ ozs. potash, and dry.

*Light Blue for Cotton Wool* (50 kilos.).—Prepare at a boil with 10 kilos. sumach, lift, whiz, and work for thirty minutes in a beck with a quarter kilo. Nicholson blue at 70° C.; take out, dissolve in the same beck 5 kilos. of alum, re-enter, work at 50° C. for fifteen minutes, whiz, and dry.

*Logwood Blue for Yarns* (5 kilos.)—Dissolve half a kilo. solid extract of logwood in hot water, and make up a beck at 36° C.; enter, and give seven turns; lift, and expose to air for eight hours. Return to same beck, and give seven more turns, and make up a new beck with 340 grms. blue vitriol; enter in this, give seven turns; wring out, and return to the logwood beck in which half a kilo. sulphate of alumina has previously been dissolved; give seven turns, return to the blue vitriol beck, rinse well, and dry.

*Vat Blue, with Catechu Ground* (10 lbs.).—Boil 1 lb. catechu in water, dissolve in it 5 ozs. tin crystals, and work in this for two hours at 62° C.; wring out, and enter in a beck of 2½ ozs. chromate of potash at 25° C.; lastly, dye to shade in a common cold vat.

*Dark Blue on Vat Ground for Twills and Fustians* (17½ kilos.).—Boil for two hours with 1 kilo. of soda ash, wring, and rinse; give it a light blue in the copperas vat, and take through water at 50° C. acidified with 1 kilo. of sulphuric acid, and rinse. Make up a cold beck with 5 kilos. nitrate of iron and 90 grms. tin crystals, and work the goods in it for one hour, and then dye in a fresh cold beck with 5 kilos. logwood and 1½ kilo. alum. If a darker shade is required, put in the spent logwood bath the solution of 40 grms. chromate of potash, re-enter the goods, and work for half an hour.

*Topping for Vat Blue Yarns* (10 kilos.).—Dye in the cold vat a medium blue, if a dark shade is required, and a light blue for a medium shade. Then take through a cold beck with a half kilo. of sulphuric acid.

Enter in a fresh cold beck made up with 2½ kilos. logwood, work forty-five minutes, and transfer to another beck of half a kilo. alum. Work here for an hour, lift, add 100 grms. tin crystals, stir up well, re-enter and work for an hour, and finally pass through water.

*Brown for Yarns and Pieces* (12½ kilos.).—Prepare with sumach, and steep over night in a beck made up with 1¼ kilo. sulphate of alumina. Dye with 5 kilos. peachwood and 1¼ kilo. fustic, saddening finally with decoction of logwood.

*Fast Red Brown* (5 kilos.)—Boil 1 kilo. cutch in water, settle, and in the clear dissolve 100 grms. blue vitriol. Work the yarns at a boil, and make up a fresh beck at a boil with 130 grms. chromate of potash. Work for fifteen minutes and rinse. Boil 1½ kilo. sumach in water, work for a quarter of an hour in the liquid at 85° C., lift, and dissolve 80 grms. tin crystals in the beck. Re-enter, work for a quarter of an hour, and wring out. Make up a fresh beck of 1 kilo. peachwood and 250 grms. alum. Work in this for an hour at 36° C.

*Brown* (100 lbs.).—Boil 20 lbs. of catechu in water; dissolve in the solution 10 lbs. of alum; let settle; enter the yarns in the hot liquid, and after working it take out and enter in a fresh beck at 212°, made up with 4 lbs. chromate of potash. Rinse and soften with oil and soap.

*Fast and Bright Brown* (10 lbs.).—Boil in water 2 lbs. genuine Pegu cutch; dissolve in the liquid 3 ozs. of blue vitriol, and make up with water to 70 litres. Let settle; heat the clear liquid to a boil, enter the yarn, and steep for two hours. Lift, and enter in a fresh boiling beck of half a pound of bichrome. Give six turns, take out, and rinse in cold water.

For a finer shade make up a fresh beck at 37° C. with half a pound of alum and 1 oz. tin crystals, and raise the yarn in it, adding, if needful, a little mageuta.

*Chamois for Cotton Wool* (25 kilos.).—Work in a cold beck with 2 kilos. nitrate of iron at 50° B., for ten minutes. Lift, whiz, loosen, work in a luke-warm beck with 2½ kilos. soda for ten minutes, take out and rinse.

*Crimson for Yarns* (5 kilos.).—Work in a weak sumach beck, and mordant with a quarter kilo. of

sulphate of alumina. Dye with 2 kilos. of peachwood for an hour; lift, and add to the beck half a kilo. of nitro-muriate of tin; re-enter, steep four hours, wash and dry.

*Fast Chrome Green for Yarns* (5 kilos.).—Ground from pale to medium blue in a moderately sharp vat; sour with 250 grms. sulphuric acid, rinse, take through warm water at 62° C., enter in a cold beck of 80 grms. chromate of potash, and give a couple of turns. Lift, and add to the beck 250 grms. sulphuric acid, stir up, re-enter the yarn, and work till even. Rinse and dry.

*Light Grey on Pieces* (60 lbs.).—Boil 1½ lb. solid extract of logwood and half a pound of extract of bark in water. Run the pieces six to eight times through, press, and run through a fresh beck of 5 lbs. copperas. Rinse and finish with the following mixture:—45 lbs. farina, 3 lbs. wax, and 6 lbs. cocoanut oil are boiled to a stiff paste. The pieces are calendered out of this mixture and pressed.

*Medium Grey* (60 lbs.).—Increase the extract of logwood to 2½ lbs. and the bark extract to three quarters of a pound, and use 10 lbs. of copperas.

*Dark Grey.*—4 lbs. extract of logwood and 1½ lbs. bark extract, 15 lbs. copperas. Add to the finishing mixture logwood liquor and copperas enough to colour it slightly. If a yellow tone is required add more bark liquor, and for a reddish shade take some extract of sapan.

*Mode Grey* (5 kilos.).—The yarn, previously cleaned, is worked for two hours in the decoction of 1 kilo. sumach and 130 grms. fustic. Take out and dye in a fresh beck with 130 grms. copperas. Top in clear solution of gentiana or methyl violet.

*Dark Macarat* (10 lbs.).—Boil 2 lbs. catechu in water; in the solution dissolve 5 lbs. sulphate of copper, and work the goods in this at a boiling heat. Leave them over night in the liquor, take out in the morning, and pass them through a beck of half a pound of chromate of potash at a boil. Lift, and soak for 30 minutes in tin solution at 2½° B. Lift, and top with the decoction of 2 to 3 lbs. of logwood at a hand heat. Work in this for an hour, lift, add 1½ oz. tin crystals, re-enter, work, wring, and dry.

*Light Olive* (5 kilos.).—Boil 1½ kilo. fustic in water, make up a beck with the extract, dissolve in it half kilo. alum, enter and steep for an hour: take out and dissolve in the beck 32 grms. extract of indigo, re-enter, and work for a quarter of an hour.

*Medium Olive* (5 kilos.).—Extract 250 grms. sumach in boiling water, enter in the clear liquid, steep, and make up a fresh beck with 250 grms. copperas. Enter the yarn previously wrung out, work it for fifteen minutes, wring out and enter in a fresh beck acetate of alumina at 1° B., give twelve turns at 62° C.; wring out, and work for half an hour in a fresh beck of 1¼ kilo. bark.

*Dark Olive Reseda* (5 kilos.).—Boil out half a kilo. sumach, and work for an hour in the clear liquid. Make up a fresh beck with three-quarters kilo. copperas, work for a quarter of an hour, wring out; give twelve turns in a fresh beck of red liquor at 1° B. at 62° C. Take out and work for an hour at 62° C. with 2½ kilos. bark.

*Light Olive* (10 lbs.).—Boil 1 lb. bark in water. In another kettle boil half a lb. turmeric, and mix the two decoctions, and dissolve in them 5 ozs. alum, and 1½ oz. extract of indigo or more, as the shade requires. Soak the yarn in this liquid at 31° C., and top with extract of Brazil wood.

*Fine Orange for Yarn* (5 kilos.).—I. Boil 630 grms. annotta in the solution of 320 grms. of soda crystals, and work in the hot clear liquid for half an hour. Take out and pass through a fresh beck of half a kilo. of alum at 28° C. If a redder shade is required, add solution of magenta. II. Steep the bleached yarn over night with 180 grms. of tannin. Take out and dye in a fresh beck at 62° with aniline orange (chrysaniline or phosphine).

*Yellow on Yarn* (5 kilos.).—Make up a mordant of red liquor at 5° B., and steep the clean yarn in it over night. Boil out 2½ kilos. of bark in water, and dye to shade in the liquid at 75° C. If a brighter shade is required, add 50 grms. tin crystals to the bark beck.

*Light Rust Yellow* (50 kilos.).—The yarn previously bleached is washed for fifteen minutes in a cold beck made up with 2½ kilos. nitrate of iron at 50° B. Take out and enter in a fresh cold beck made up of 2½ kilos. of soda-ash. Work for fifteen minutes, hang out to the air, and rinse. For heavier shades repeat these operations twice.

*Dark Rust Yellow* (50 kilos.).—Boil up 5 kilos. of yellow rosin, soap with 2 kilos. annotta and 1 kilo. young fustic. Steep the goods for thirty minutes in the boiling liquid.

*Blue Black on Velvets* (50 kilos.).—After cleaning lay the goods for three hours in a hot beck of 5 kilos. sumach; lift, and steep thirty minutes in cold black liquor at 3° B. Lift, spread out to air, and enter in a fresh cold beck with 70 grms. chromate of potash. Rinse, and dye in a fresh beck with 1 kilo. logwood, entering at 75° C., and raising the temperature by degrees.

New Colours on Cotton—*Alizarin Puce.*—Prepare a chrome mordant as follows:—Set up a stoneware bowl, holding 30 litres, in the open air or under a good draught, and heat gently. Put into it 3 kilos. chromate of potash in coarse powder, 4·4 litres of boiling water, 2·6 litres of nitric acid at 36° B. Stir well together, and add gradually 0·72 litres of white glycerine at 28° B., and 4·28 litres of acetic acid at 7° B. When the whole is dissolved pour into a double-bottomed copper pan, and heat to a boil with steam. Keep up the heat till the liquid in thin layers appears of a fine green. Then allow it to cool in a stoneware bowl, decant, wash the deposit of saltpetre in 0·8 litre of cold water, and add the washings to the clear liquid. The cotton is worked, or in case of pieces padded in this liquid, dried, passed through water containing $\frac{1}{10}$th of ammonia, washed, and dyed with alizarin.

*Aniline Blacks.*—With regard to these colours, Roscoe says* :—

* Royal Institution Proceedings, June, 1876.

"In the year 1860 John Lightfoot, calico printer, of Accrington, applied to the processes of calico printing a black colouring matter which had been previously obtained in the manufacture of mauve from aniline by Roberts, Dale, & Co., of Manchester.

"This black colouring matter is invariably formed when either aniline or toluidine, or mixtures of these two substances, are subjected to oxidizing actions; but in spite of several researches which have recently been published on aniline black, we are as yet unacquainted with its chemical formula, nor indeed can we say that it even possesses a constant chemical composition.

"In order that a colouring matter shall be fixed or permanent, it must be fastened in some way to the fibre of the cloth. In the case of cotton this is generally effected (1) either by the precipitation of the soluble colouring matter in the fibre by means of a mordant, which forms an insoluble compound termed a lake with the colour, as in madder dyeing and steam-colour printing; or (2) by the fixation of the colour by means of albumin, as in pigment printing; or (3) by the gradual oxidation and consequent precipitation of the colouring matter in the fibre, as in indigo printing. It is to this latter class of processes that aniline black dyeing or printing belongs; for the aniline salt under the action of certain oxidizing agents passes more or less quickly from the condition of a colourless solid readily soluble in water, into that of a black amorphous insoluble powder not to be distinguished at first sight from soot. Hence if the cloth can be impregnated with the aniline and with the oxidizing agent at the same time, and if the process of oxidation can be allowed to go on in the fibre, the black will be formed, and will be permanently fixed in the fabric.

"Many oxidizing agents, such as chlorine, ozone, or electrolytic oxygen, have the power of transforming aniline into this black pigment. In most cases a high temperature is needed for this purpose. Thus, for instance, if aniline is heated with chlorate of sodium, and if then hydrochloric acid be carefully added, a deep black almost solid mass is produced. In order, however, that the process may be employed in dyeing and calico printing, it is absolutely necessary to avoid high temperatures as well as the action of strong acids, because when exposed to these the cloth invariably is rotted or becomes "tender." If a mere mixture of aniline salt and chlorate of potash be heated strongly enough, the black is formed; but the heat necessary to produce the colour is sufficient, together with the hydrochloric acid which is at the same time liberated by the decomposition, to make the cloth rotten, and therefore to render this process useless.

"It was found by Lightfoot that if an addition of 4 ozs. of nitrate of copper solution was made to the pound of aniline and to the chlorate, the oxidation of the aniline went on at a lower temperature than when the copper salt was absent, and hence, when carefully worked, the black could be formed by this process without tendering the cloth. Certain technical objections to this process, however, soon arose; and in 1865 Lauth proposed to use the insoluble copper sulphide instead of the soluble nitrate, by which means he prevented the deposition of the copper on the "rollers" and on the "doctors" which took place in Lightfoot's process. The method thus modified has been and now is extensively used for the production of black, and the chief, if not the only objection which can be urged against it is that the black thus obtained is not perfectly permanent, but is liable to become green when exposed to reducing agents, such as the sulphurous acid contained in the impure air of our towns. This is, however, a serious drawback, and one which those practically engaged in solving such problems have not been able to remove. So much so indeed is this the case, that it is generally believed that the property of aniline black to become green when exposed to sulphurous acid, and to return to the black when treated with alkalies, is an essential property of the substance, which may be compared with the property of litmus to change colour in presence of acids and alkalies.

"That the aniline black can not only be produced in presence of copper, but also, as Lightfoot showed in the year 1871, in presence of vanadium salts, and that by vanadium alone can the black be obtained of the requisite permanent character, has now been proved beyond doubt. Moreover, the quantity of the vanadium necessary in order to produce the oxidation of the aniline is about one thousand times less than that of the copper. Thus, if a piece of calico be dipped into a solution of 2·5 grains of vanadate of ammonia dissolved in 1 gallon of water and then dried, the cloth thus prepared is capable of producing an intense black if treated with the mixture of aniline salt and chlorate. In the same way if 1 gallon of colour be made containing 20 ozs. of aniline hydrochlorate, 10 ozs. of chlorate of soda, and 3 grains of vanadate of ammonia, a mixture is obtained with which no less than from 20 to 25 pieces, or from 500 to 600 yards of cloth, such as that exhibited, can be thus printed of a permanent black.

"In dyeing, also, the vanadium will be extensively used; and in the same way only mere traces of this rare metal are requisite, whereas the copper black cannot be used for dyeing. Thus, for instance, 1 gallon of colour intense enough to dye 40 lbs. of cotton yarn black is obtained by mixing 8 ozs. of aniline hydrochlorate, 4 ozs. of sodium chlorate, and 8 grs. of vanadate of ammonia. Cotton, wool, or silk dipped twice into this mixture and then aged, or allowed to oxidize, and "raised" in a solution of carbonate of soda, is dyed a deep rich and permanent blue black. The goods may also be allowed to steep in a bath of the above strength for three days, then well washed in warm water, or boiled in a weak solution of acetic acid, to remove any bronze colour found on the surface of the silk or wool. The permanent black is then formed, and the fibre found to be quite strong.

"The part played by vanadium in the formation of the black colour may be easily explained, when we

remember the ease with which the metal passes from one degree of oxidation to another; thus from $V_2O_5$ the highest degree, to $V_2O_4$, and *vice versâ*. In this way it doubtless acts, as M. Guyard has suggested, as a carrier of the oxygen of the chlorate to the aniline, being alternately reduced and reoxidized, so that an infinitely small quantity of vanadium compound will convert an infinitely large quantity of aniline salt into aniline black, reminding one of the action of nitrous fumes in the leaden chamber.

"Some time after the discovery of aniline black, Robert Pinkney, of the firm of Blackwood & Co., of London, discovered, independently of Lightfoot, that vanadium can be most advantageously substituted for copper in the formation of aniline black; and he employed this reaction for the preparation of a permanent marking ink termed 'Jetoline,' of which many thousand of bottles have been sold. A few grains of vanadium—say from seven to twelve—are sufficient to produce, together with hydrochlorate of aniline and chlorate of soda, a gallon of marking ink.

"The subject of the use of vanadium as a valuable dyeing agent was next taken up by the Magnesium Metal Company, of Patricroft, near Manchester; and thanks to the unwearied exertions of S. Mellor, this firm have now succeeded not only in securing a very considerable supply of the rare element which occurs in the Keuper sandstone as the new mineral Mottramite, but are now in a position to produce a vanadium black for both calico printing and dyeing which is perfectly permanent. This is the more remarkable, as up to this time no aniline black made with copper has been produced in commerce which will withstand the reducing action of sulphurous acid.

"As the result of a large number of experiments made with various qualities of commercial aniline, and by varying the strengths of solutions, proportions of aniline and sodium chlorate employed, and also by altering the temperature and the conditions of ageing, Mellor has found (1.) that within certain limits the purer the aniline used the deeper and more permanent is the black obtained. (2.) That there is a maximum density of colour, beyond which, if larger proportions of aniline salt and chlorate are used, corresponding advantages of colour are not obtained. This maximum colour is yielded by 16 ozs. to 20 ozs. of hydrochlorate of aniline per gallon of colour. (3.) That for the formation of a permanent black, the amount of aniline salt and sodium chlorate used for 1 gallon of colour must bear a definite relation to each other, the weight of sodium chlorate being about one half that of the aniline hydrochlorate used. (4.) That the permanency of the black depends very much upon the care and skill shown in 'ageing' the cloth. If the cloth is aged in a moist atmosphere a blue-black is developed, which is very fleeting; but if aged in a dry air, and at a high temperature, a permanent black is obtained. It is also interesting to learn that for other colours also, the use of vanadium appears to be of value, as in the production of catechu browns as well as in some of the brighter aniline dyes."

*Aniline Black.*—The following processes are at present in use. The goods are stretched out tightly, and exposed to the spray of solutions of a salt of aniline and of the bichromate of potash. The spray is applied by means of a horizontal brush, to which a reciprocating motion is given by suitable machinery. The cotton takes at first an intense green, but becomes a full black on washing and passing through a soap beck. A mixture of equal measures of bisulphate and bimuriate of aniline gives the best results, and the bichromate solution should contain 10 per cent. of the solid salt.

*Aniline Black.*—Müller-Pack prepares protochloride of iron by dissolving 3 parts of iron in a mixture of 10 parts muriatic acid and 10 of water, and lets the solution down to 17° Tw. In this the yarn is steeped for two hours, and is then aired for twelve hours. Meantime a solution is made of 3 parts aniline in 5 parts muriatic acid and water, and $2\frac{1}{10}$ parts of chlorate of potash are added, previously dissolved in 30 parts of water. In this mixture the yarn is steeped, and is then heated in a covered vessel gradually to from 30° to 50° C., and is then hung out to the air. It is next taken through a beck of bichromate of potash. If this black is passed through weak sulphuric acid and then through water and weak caustic soda it takes a bluish tone.

*Aniline Blues.*—If about to dye with diphenylamine blue (the sulpho-conjugated salt of the blue being a compound of lime or baryta), work the cotton in solution of tannin at 3 per cent.; pass through the solution of the blue, dye in water, and dry.

If alkaline blues are employed, the sulpho-conjugated salts of which are soda or ammonia compounds, take for 10 kilos. of cotton a solution of tannin containing 3 per cent. of the weight of the cotton; boil for fifteen minutes, wring, and pass into a beck of $1\frac{1}{2}$ kilo. alum, a quarter tartar emetic, three quarters soda crystals, and a quarter tartaric acid. These wares are all dissolved separately, and the solution of the blue is added last. Heat to 65° to 70° C., enter the cotton, and dye, letting the temperature sink by degrees. The beck may be used continuously, adding more mordant as it becomes spent. It is best to dye first heavy shades in the beck, then mediums, and then light shades.

For saffranin and the aniline greens the goods are passed first into a beck of perchloride of tin at 2° B., wrung, passed into a tannin beck, wrung again, and entered in the dye beck.

Cotton may also be mordanted in a solution of nitrate of urea (2 grms. per litre of water), boiled, wrung, passed into a solution of biphosphate of lime (5 grms. per litre of water), wrung, and entered in the dye beck. From this manner very bright shades may be obtained with almost all the anilines.

*Guernsey Blue for Yarns* (10 lbs.).—Prepare with 2 lbs. sumach, and dye at 32° C. with the solution of 2 lbs. Guernsey blue; lift, add 1 lb. alum, give the yarn a few more turns, take out, and dry.

*Fast Aniline Blue for Yarns* (5 kilos.).—Steep for

three hours in a hot beck of 250 grms. of tannin; wring, and enter in bichloride of tin at 4° B. for two hours; rinse, and let lie over night. The next day enter in a beck of half a kilo. curd soap at 75° C; work for an hour, lift, and make up the dye beck with aniline blue (not Nicholson's) and a little sulphuric acid. Heat to 50° C.; and enter, raising slowly to a boil. Dye rather darker than the pattern; wring, and pass through a beck of half a kilo. curd soap at 75° C.; rinse, and take through a beck of half a kilo. alum; dye without rinsing.

*Deep Bismarck Brown on Velveteens* (40 to 45 lbs.).—Run through decoction of catechu at 4° Tw. and 180° Fahr.; raise with solution of bichromate of potash at 2° Tw. and 150° Fahr.; wash off, and take through 60 gals. fustic liquor; lift, drain, and stove dry; singe, and repeat the catechu, chrome, and fustic, and stove as before. Enter in a beck of Blackley brown at 170° to 180° Fahr.; 8 to 10 ozs. of colour gives a good red shade. The fustic liquor should contain 1 lb. fustic to 3 gals. water.

*Eosin Pinks and Roses* (10 lbs.).—Work in a hot beck made up with 1 lb. of curd soap, and then soak in a fresh beck of 4 lbs. sugar of lead. Repeat both these processes twice or thrice, according to the shade required. Lastly, work in the colour dissolved in water.

*Pomona Green.*—Work in a tannin beck, or in an extract of gall-nuts or myrobalans. Lift, and run through a very dead double muriate of tin. Take through cold water, and then work in a cold solution of the colour.

Linen is steeped for twelve hours in a beck made up of tannin or decoction of galls. Next work in acetate of alumina, and then dye to shade in a beck of iodine green.

*Iodine Green.*—Prepare with tannin, rinse, and dye at 50° C. The colour should be dissolved at 60° C., avoiding higher temperatures.

*Night Green on Velveteens* (1 piece).—Boil 3 lbs. of galls in 4 gals. water. Settle, draw off the clear, mix with 20 gals. water, heat to 150° Fahr. in the jigger, and run the piece six times through. Add 1 pint of double muriate to the solution, and run the piece through again. Wash, and run it six times through a beck of 4 gals. fustic liquor and 20 gals. water. Then add 4 quarts of alum liquor, at 8° Tw., and run the piece several times through this; lift and dry. Make up a jigger with 20 gals. water and half a pound of pomona paste previously dissolved. Run through till all the colour is taken up.

*Turkey Red with Artificial Alizarin.*—Give one oiling less than if the goods are to be dyed with madder or garancin. The tannin bath is also dispensed with. The alumingis performed in the ordinary manner with the following mordant:—To 50 kilos. of crystallized alum take 15 kilos. of soda crystals and mix their solutions in water, stirring well. The clear liquid is finally set at 5° B. The yarns are steeped for one day in this liquid and are then very carefully washed and wrung out, and are ready for the dye beck. This is made up of alizarin and tannin, half a kilo. of the latter to every 50 kilos. of cotton. If the water contains no lime, 100 grms. of chalk are added for every 50 kilos. of cotton. Begin to dye with a perfectly cold beck, raise the temperature gradually for two hours to the boiling point, and finally boil for one hour. The dyed yarn, without any clearing, is at once bloomed with curd soap and annotta. Treatment with tin crystals is only needed for rose shades.

*Saffranin Ponceau and Scarlet* (5 kilos.).—Prepare a boiling hot beck with half a kilo. turmeric, and work the cotton in it for an hour. Lift, drain, and take through a beck with half a kilo. sulphuric acid. Work for three hours at a boil with 1 kilo. sumach, wring and dye in a fresh beck at a hand-heat, with a clear solution of saffranin.

*Saffranin Pinks and Roses.*—Wash well with soap and work for two hours in a cold solution of sugar of lead at from 5° to 6° Tw. Wring out, and work in a strong soap beck at 60° C. Rinse, and dye in the solution of saffranin in water at 65° C.

*Saffranin Rose for Yarns* (5 kilos.).—Mordant with 1 kilo. sumach, and dye in a clear solution of saffranin. If a more blue shade is desired add 50 to 76 grms. of tin crystals to the sumach beck.

*Croissart and Bretonnière's Patent Colours.*—When using these colours for grey, silver grey, and brown, it is almost impossible to get the shades uneven. It seems further as if the fibre becomes animalized, and forms a ground upon which aniline grey or other aniline colours take readily.

*Silver Grey* (20 kilos.).—Two becks are required, both at a boil. *Beck* I.—Patent colour No. 1 of the Göttingen works, more or less according to shade. II. *Fixing Beck.*—1 litre of red liquor at 10° B. Enter in I., then in II.; lift, add aniline grey, and dye to shade.

*Grey* (25 kilos.).—2½ kilos. of patent colour No. 1. Fixing beck: 2 kilos. copperas and 1 kilo. blue vitriol.

The flat is preserved, and strengthened with 100 grms. of patent colour No. 1 for the next lot.

*Brown* (25 kilos.).—3 kilos. of patent colour No. 18. Let steep over night in the hot liquid. Lift, and take through the clear solution that remains when a quarter of a kilo. of chromate of potash and half a kilo. of copperas are mixed and allowed to settle.

*Sky blue with Lo-kao.*—Dissolve in a bath of hyposulphite of soda. A fast light blue is obtained, not affected by light. In an ammoniacal solution it gives a violet on cotton without a mordant.

Linen and Jute.—*Bleaching Linen* (100 lbs.).—Make up a boiling solution of 25 lbs. quicklime and 12 lbs. soda ash. Let cool, enter the yarn, and steep in the cold for twelve hours. Take out, rinse, and pass through weak sulphuric acid. Rinse again; stir up 8 lbs. good chloride of lime in water, let settle, and enter the yarn and steep till perfectly white. Lift, rinse, and pass through weak muriatic acid. Dissolve 2 lbs. curd soap in boiling water, add as much ultramarine as may be required for a blue tint; stir well up, enter the bleached yarn, take out, and dry.

*Black Linen* (40 lbs.).—The goods are made perfectly clear and steeped for an hour in the solution of 4 lbs. solid extract of logwood. Squeeze well, and take eight times through a cold beck of 7½ ozs. bichromate and 12 ozs. blue vitriol. Squeeze, and dissolve in the first bath 1 lb. soda ash. Heat to 75° C., squeeze again, and dissolve in the bath 1 lb. copperas. Work for half an hour, and rinse. To hinder the goods from smearing, take through water in which a little gum has been dissolved.

*Greenish Mode Grey Linen* (10 kilos.).—Dissolve one-half kilo. soda-ash in water, and make up so that the linen can lie in the liquid, and boil for an hour. Wash, and take through a beck of one-half kilo. sulphuric acid, and wash again. 1 kilo. chloride of lime is stirred up to a cream with water, let settle, and the linen is steeped in the clear liquor for six hours, with occasional turning. Lift, and take through cold water to which 1 kilo. muriatic acid has been added. This preparation is needed for all light colours. Boil out one quarter kilo. sumach, and 1 kilo. bark. Work in the clear liquor for one hour, wring, and put in a fresh beck of one quarter kilo. copperas. Work for fifteen minutes, and pass through water. Top in a beck of 1 kilo. alum at 50° C., and add by degrees very small doses of bark liquor and extract of indigo, till the shade is obtained. Rinse, and dry.

*Magenta on Linen Yarn.*—Prepare with 5 lbs. olive oil, 1 lb. sulphuric acid, 10 lbs. water, and 10 lbs. methylated spirit at about 60° Fahr., and let steep for three hours, wring, and drain. Then add one-quarter lb. vitriol, and pass the yarn five times through the liquid, wring, and enter in a magenta beck at 140° Fahr.

*Red, Fast Sanders, on Linen Yarn* (100 lbs.).—Ground slightly with annotta; mordant by steeping over night in perchloride of tin at 8° B. Rinse, and wring, and enter in a beck made up with 5 lbs. of sanders, and work at a boil for twenty minutes. Take through sulphuric acid at ½° BEAUMÉ, wring, and rinse.

*Brown on Jute* (5 kilos.).—Boil out 1 kilo. catechu in water, and dissolve in the clear liquid 100 grms. of blue vitriol. Steep the jute in this at a boil for two or three hours. Lift, and make up a beck at a boil with one quarter kilo. chromate of potash; take the jute through this, and then through water. Top in a fresh beck with 5 grms. Bismarck brown (aniline), 130 grms. alum, and one half kilo. logwood.

*Cherry Brown* (5 kilos).—Boil 1 kilo. of sumach, and work for an hour in the clear boiling liquid. Lift, and dissolve in the beck 50 grms. tin crystals; enter again, and work for fifteen minutes. Lift, and make up a fresh beck with 1 kilo. logwood, 80 grms. magenta, and 400 grms. alum. Work for an hour in the cold liquid, lift, add to the same beck 80 grms. chromate of potash, re-enter, work for thirty minutes, and rinse.

*Light Brown on Jute* (25 lbs.).—Dye hot with 2½ lbs. catechu and 4 ozs. blue vitriol. Lift, and enter into a hot beck of from 4 to 6 ozs. bichrome, according to shade, and give two or three turns.

For a medium brown, to the same quantity of yarn use 5 lbs. catechu, 8 ozs. of blue stone, and 12 ozs. bichrome.

*Dark Brown on Jute* (25 lbs.).—Work hot with 5 lbs. catechu, 6 ozs. alum, 8 ozs. blue vitriol, and 4 lbs. logwood. Lift, and give two or three turns in a beck of from 8 to 12 ozs. bichrome. If not dark enough, enter in a logwood beck with one quarter lb. alum. If a redder tone is required top with magenta in a separate beck.

*Aniline Green on Jute* (25 lbs.).—Prepare with 5 lbs. myrobalans; then work in a red liquor made from 4 lbs. alum and 22½ lbs. sugar of lead, using the clear only; wring, and dye in the solution of aniline green.

*Light Green on Jute* (5 kilos.).—Boil out one quarter kilo. sumach, and steep for three hours in the clear boiling liquid. Lift, and make up a cold beck with methyl green. Enter the jute, and work till the colour is even. For yellower shades add picric acid.

*Prussiate Green on Jute* (5 kilos.).—Make up a boiling beck with 1 kilo. extract of bark, and as much alum. Steep for an hour, lift, and prepare the two following becks:—I. 250 grms. nitrate of iron; 40 grms. tin crystals. II. 136 grms. yellow prussiate. Work in I., then give five turns in II., lift, and add to II. 250 grms. sulphuric acid, and give five turns. Work for thirty minutes in acetate of alumina at 2° B., and dye up in a fresh beck of extract of indigo and a little bark.

*Aniline Green for Jute Yarn* (45 lbs.).—Work for an hour in the hot decoction of 5 lbs. myrobalans; mordant with 4 lbs. alum and 2½ lbs. acetate of lead, using the clear only. Let it steep for two hours, and then dye with the solution of aniline green.

*Orange on Jute.*—Mordant the yarns with basic acetate of lead; wring, enter in lime-water, give six turns, and wring again. Enter in a bichrome beck of 1½ lb. to 2 lbs., with 1½ lb. sulphuric acid. Wring, and enter in boiling lime water; give three turns, lift, and wash.

*Red on Jute* (5 kilos.).—Steep for an hour in the decoction of 250 grms. tannin at 90° C. Lift, and make up a beck with 80 grms. aniline orange at 60° C., and dye. Lift, add the clear solution of 40 grms. saffranin to the beck, re-enter, and dye to shade. (An expensive colour.)

*Yellow on Jute* (5 kilos.).—Bleach, and enter in a cold beck of 80 grms. sugar of lead, and work for fifteen minutes. Lift, and work for the same time in a cold beck of 80 grms. chromate, and rinse. If a redder tone is required, work lastly in weak magenta.

PREPARING AND DYEING OF SILK.—Silk is banded in the same manner as cotton, using no particular number of hanks, but in quantities convenient for making up into skeins when finished. After banding, it is carefully tied up and put into fine canvas bags, and seethed in these in a strong solution of soap for three or four hours, until all the gum is boiled off. If the silk be yellow gum, it is put upon sticks like the cotton, and wrought in a solution of

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